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Laser-Induced Graphene-like Carbon for Volatile Organic Compound Sensing

Thesis presented by

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Abstract

Laser-induced graphene-like carbon (LIG) is a potential resource-efficient fabrication route to support the abundance of sensors required by Industry 4.0 for IoT edge sensing applications, including wearables and worker safety LIG is formed *in situ* by laser irradiation of suitable precursors, e.g. polyimide, to yield conductive, porous, 3D foams comprised of graphene sheetlets. This direct conversion allows for good spatial resolution ($\sim 50\ \mu\text{m}$) and arbitrary pattern design, thus enabling the prototyping of diverse devices ranging from supercapacitors and interdigitated electrodes to electrochemical and Volatile Organic Compound (VOC) sensors.

This thesis develops resource efficient, iterative system-agnostic optimisation procedures for LIG fabrication and novel back-contacting routes. Iterative use of design of experiments optimisation provides robust investigative route to determine ideal conditions with minimal investment of time and resources. An all-laser process of achieving back contacts from LIG to underlying metal was also demonstrated. Unlike current mechanical or silver paint contacts, back-contacts decouple the mechanical and electrical interface to external electronics, thus improving system reproducibility and, preventing surface contamination of the active material. Further, this scalable approach is a promising device integration route for both wafer-scale and printable electronics.

Low-resource, low-power chemiresistive VOC sensors are also reported, comprised of low mass loadings of SnO nanoflowers (synthesised below 100°C and at ambient room pressure) on LIG electrodes. These offer a low-energy alternative to standard VOC sensors, which typically require high operational and fabrication temperatures ($>300^\circ\text{C}$). These chemiresistive sensors can detect methanol vapor at laboratory temperature, with a limit of detection ($170\pm40\ \text{ppm}$), below 8-hour exposure levels for worker safety (200 ppm). The sensors also demonstrated stable DC resistance responses $\Delta R/R = 9 \pm 2\%$ to 710 ppm of methanol for over 21 days in ambient conditions.

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Declaration

This is to certify that the work I am submitting is my own and has not been submitted for another degree, either at University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism and intellectual property.

Richard Murray

Date

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1.1 Thesis Overview

This thesis investigates LIG for its applicability in VOC sensing. This will be discussed in terms of the fundamental properties of LIG, its fabrication and integration into practical systems. Subsequently, the functionalisation of LIG with separately prepared nanoparticles yielding a VOC sensor is demonstrated for the first time. The challenges addressed are tabulated in Section 5.2.

Chapter 1 gives an overview of the applicability of low-resource cost VOC sensors in human health monitoring, food packing and worker safety applications. It further summarises the prevailing literature about LIG, its properties and formation processes and the challenges for its development as a mature material platform. Brief synopses of chemiresistive gas sensing theory, contact resistance optimisation routes and Raman spectroscopy there were also included as a primer for the interpretation of the experimental chapters. These topics are further discussed in the thesis appendices.

Chapter 2 and the associated supplementary information focuses on the resource-efficient material optimisation of the LIG platform material using iterative design of experiments methods demonstrating its application to two CO₂ laser systems. This shows a generalisable method to produce application-specific optimised LIG in a system-agnostic manner, focusing on a low-sheet resistance demonstrator. This work: challenges the necessity of high cost laser systems for preparing LIG, seeks to reduce the high resistance of produced LIG material, seeks to systematise the *ad hoc* One-Factor-at-a-Time (OFAT) optimisation methods currently applied to the complex optimisation space and expand the limited knowledge surrounding the impact of different laser parameters on LIG quality. This work appears as published in ACS OMEGA 10.1021/acsomega.1c00309 along with its associated supplementary information.

Chapter 3 and the associated supplementary information follows the back-contacting of LIG material, via an all-laser fabrication process to produce robust and reproducible electrical contacts, with minimal contact resistance. Here we demonstrate novel, scalable contact methods which would allow for the facile integration of resulting devices. This work challenges the high-

resource cost and unscalable contemporary silver paint-based contact method for LIG. However, there is still no conclusive optimal contact metal, even pristine graphene, and polyimide on arbitrary metal films is not commercially available. Finally, this work investigates the known complex system dependence for LIG formation, with the additional complication of metal sub-layers. This work appears as published in IOP Nanotechnology 10.1088/1361-6528/ac7c7b along with its associated supplementary information.

Chapter 4 and the associated supplementary information builds on the material optimisations of Chapters 2 and 3 to produce a resource-efficient ambient temperature VOC sensor. These sensors are produced by the dropcasting of separately prepared SnO nanoflowers, to produce a chemiresistive sensor composed of a p-type granular network on a graphitic supporting electrode. This work addresses the challenges of contemporary VOC sensors: the critical raw materials required and associated high temperature fabrication route, the high resource cost electrodes, the high operational temperature ($>350^{\circ}\text{C}$) and prohibitively expensive VOC gas sensing systems required. This paper appears as it was submitted to Sensors and Actuators B, along with its associated supplementary information, but it has not yet undergone peer review.

Chapter 5 reflects on the findings of the experimental chapters, their context and impact, and discusses avenues for fruitful future work, e.g. transfer of developed techniques onto biopolymer biomaterial feedstocks, adaptation of back contacting methods to biodegradable metals and the extension of low-resource VOC sensors towards smart-sensor arrays.

1.2 Project Motivation

VOCs are a silent, unseen risk in everyday life. They can originate from industrial processes ranging from pharmaceutical manufacturing to automotive applications; as by-products of combustion, fuel storage and cooking; and even outgassing from household furnishings [1–7]. They can also accumulate in enclosed spaces, or areas with poor air exchange, resulting in increased local concentration and associated cumulative exposure risks [8, 9].

Typical industrial monitoring still relies on periodic spot checking of atmospheric conditions within work spaces, often times by collecting gas samples for laboratory based assessment, e.g., gas chromatography. These analyses focus on benzene, toluene, ethylbenzene and xylenes, due to their proliferation in industrial applications, emission in vehicle exhaust and carcinogenic nature, even at ppb levels [10].

In addition to the those already mentioned, there are other commonly used VOCs, both industrially and domestically. These include alcohols (e.g. methanol, ethanol, isopropyl alcohol), ketones (e.g. acetone), cyclohexane and ammonia. These also pose a significant risk to human health at concentrations below human perception, e.g., 8-hour worker safety threshold for methanol (200 ppm) vs. human odor detection ($>10,000$ ppm) [11–14].

Viable, low-cost, point of use VOC sensors are of great interest beyond industrial safety monitoring. VOCs can also be observed as a by-product of food spoilage or as a symptom of disease [15–23]. This provides clear additional use-cases in smart food packing and for medical diagnosis. Of the top ten annual causes of death, seven have been demonstrated to produce characteristic VOCs. These include ischaemic heart disease (NO_x), lung cancer (mixed alcohol fingerprint), and diabetes (acetone). Through the detection of these VOCs, it is possible to detect these conditions before the manifestation of adverse physical symptoms as has been shown in the case of lung cancer (fingerprinted alcohol mixture), where early stage detection was achieved beyond what is possible through invasive, painful and time consuming traditional methodologies.

However, despite significant developments, conventional VOC sensors still often require elevated operating temperatures ($>300^\circ\text{C}$), which pose significant challenges for low-power, wearable sensors suited to worker safety and human health monitoring. Further, chemiresistive VOC sensors are typically produced using resource-intensive semiconductor fabrication pro-

cesses, often involving critical raw materials, thus increasing their environmental footprint [24]. Additionally, high-temperature processing steps are often required to produce the correct phase of the MOX materials and/or to calcinate previously synthesized MOX nanoparticles [25, 26]. This combination of high operational energy and resource costs have limited the uptake of chemiresistive VOC sensors. Therefore, there is a great demand for low-resource, and low-energy of operation, VOC sensors, not only for worker safety but also for disease detection and food spoilage monitoring.

This thesis demonstrates resource-efficient optimisation of a LIG-based sensing platform, via the development of novel back contacting methods to produce reliable electrical contacts. Subsequently, a hybrid LIG-nanoparticle VOC sensor was developed, capable of detecting methanol under ambient conditions, without heating or pre-treatment and without using critical raw materials at concentrations below worker safety levels (170 ppm vs. 200 ppm). This was achieved by the drop cast decoration of LIG electrode structures using SnO nanoflowers, synthesised via a low energy reflux process.

Beyond the development of a VOC sensor, this work provides a robust design and optimisation methodology for LIG and has matured the polyimide LIG platform substantially, providing material suitable for other electronic systems including, but not limited to, electrochemical sensors, strain/pressure sensors, light sensors and integrated heaters. These optimisation methods can be directly applied for adjacent, biopolymer/biomaterial feed stock materials, currently under investigation, i.e., cork and chitosan, although this was beyond the scope of this work [27, 28].

1.3 Laser Induced Graphene-like Carbon

The understanding and discussion of LIG, borrows substantially from that of graphene, due to their similarities. A brief overview on graphene, its properties, its manufacturing routes and its limitations are therefore included here to provide a basis for the discussion and understanding of LIG in section 1.3.2.

1.3.1 Graphene

Since their discovery, graphene and graphene-like materials, have been an exciting area for investigation for material science. Their popularity stems from their high carrier mobility, thermal conductivity, tensile strength, zero bandgap, high specific surface area and ballistic transport [29–35]. These idealised properties are present mainly in the mechanically exfoliated form. This limits their utilisation to enhancing material properties as dispersions in other materials and sensing applications [36–38], due to the micron-scale size of transferable sheets of mechanically exfoliated mono-layer graphene. A schematic representation of graphene is shown in Fig. 1.1.

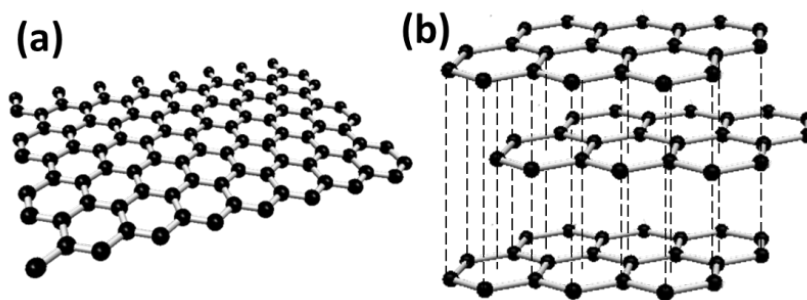


Figure 1.1: a) Graphene is a single layer honeycomb lattice of carbon atoms. b) Graphite viewed as a stack of graphene layers. Reproduced from *Lee et al. 2013* [39].

Subsequently Chemical Vapour Deposition (CVD) growth of graphene has been achieved. However, the materials properties of the material are diminished relative to the mechanically exfoliated form. This is due to the incorporation of structural defects and variability in the CVD growth method. Further, the standard synthesis method includes the deposition of a poly(methyl methacrylate) (PMMA) handling layer to assist in the removal of the supporting growth metal. The residue associated with the handling layer cannot be fully removed, as standard techniques

such as plasma etches or ashing would result in damage to the graphene sheet. These influences are shown schematically in fig. 1.2.

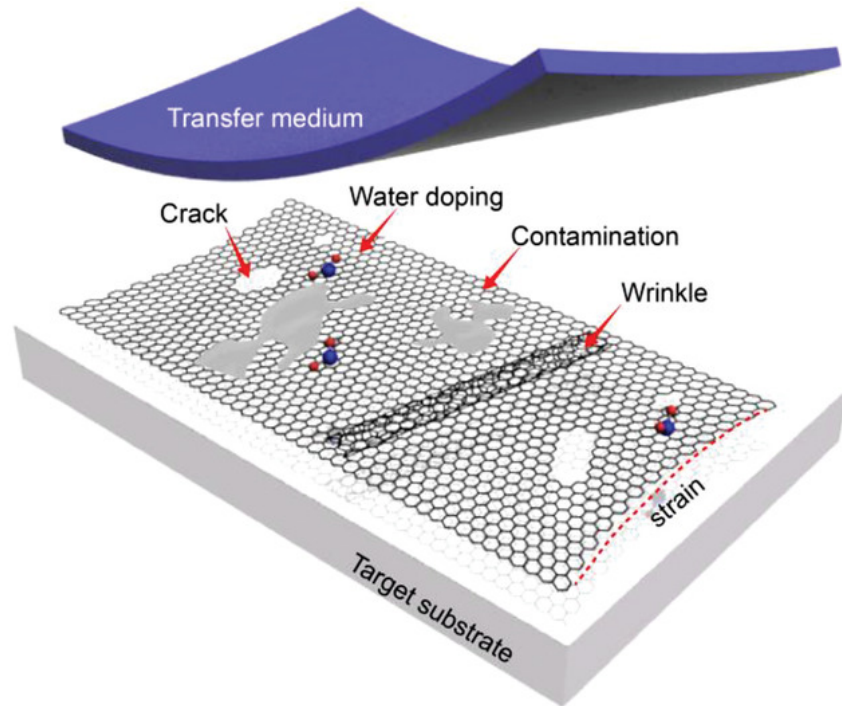


Figure 1.2: Schematic illustration of the as-transferred graphene film on target substrates with the assistance of transfer medium, highlighting the issues of cracks, unintentional doping from water molecules, contamination, wrinkles, and strains. Reproduced with permission from *Song et al.* 2021 [40].

This residue has been observed to result in uncontrolled doping of the underlying graphene sheet and prevents direct contact of the sheet. This further increases the modification of CVD-graphene from the idealised mechanically exfoliated-graphene. Mechanically-exfoliated graphene is used as a common baseline comparison material for other methods. Many graphene-based devices utilise CVD-graphene due to its ease of fabrication in semiconductor manufacturing compatible methods. As such, it has attracted significant interest for Graphene Field Effect Transistor (GFET) applications [41, 42].

The implementation of CVD growth of graphene displaying similar, although attenuated, material properties to pristine, mechanically exfoliated graphene suggests that other graphene-like materials could be used in its place. One group of methods that have gained popularity is the reduction of graphene oxide. These methods involve oxidising graphite to allow for large scale sheet separation, followed by reduction of the sheets to restore the pristine-graphene behaviour. This method would, in theory, allow for large scale production of mono-layer graphene material,

without the need for expensive deposition techniques. However, the reduction of the graphene oxide is never complete. As such, the resulting graphene-like product will contain increased levels of defects, in addition to the presence of functional groups, e.g. OH, C=O, that would modify the material's band structure, diminishing its material properties from the pristine-graphene ideal. This modification is seen to be more extreme than that of the CVD growth.

Expanding on the mechanical exfoliation approach, liquid-phase exfoliation methods, using appropriate solvents and ultrasonic waves achieves large scale separation of graphene platelets, in a solvent medium [43]. As seen with other alternative synthesis methods, the liquid-phase exfoliation results in a modulation of material properties associated with the reduced particulate size and solvent interaction and contaminant effects. This is similar to the reduced graphene oxide material, acting as a method to produce large volumes of graphene-like materials, although with diminished material properties. Its main advantage is that it produces material that is readily converted into patternable conductive inks, as a method to produce low metal sensors. Unfortunately, these inks require curing processes. Further, the conduction method requires the transfer of charge carriers from platelet to platelet of patterned graphene resulting in poor sheet resistance despite the high quality of each individual flake.

Each alternative to pristine graphene, has a trade-off in terms of ease of fabrication and material properties. Pristine mechanically exfoliated graphene monolayers demonstrate a sheet resistance of $\sim 6 \text{ k}\Omega/\text{sq.}$, when measured in vacuum. However, it is observed that for that this becomes $\sim 500 \text{ }\Omega/\text{sq.}$ for air-stable CVD-graphene devices, due to adsorbate doping from ambient water vapour and process residue [44–46]. Similarly, due to small crystallite size (35 – 600 nm), and process-induced basal plane and edge defects, liquid phase and reduced Graphene Oxide (rGO), demonstrate sheet resistances of ($\sim 2 \text{ k}\Omega/\text{sq.}$) [47,48]. In these instances the presence of defects and surface dopants result in the deviation from the zero band gap, semiconductor nature of pristine monolayer graphene.

1.3.2 Laser-Induced Graphene-like Carbon

The families of graphene and graphene-like materials described above show a range of material properties. Each material occupies a distinct niche appropriate to different applications and

presents its own challenges for optimisation. This work focuses on an *in situ* synthesis technique whereby no additional process steps or curing processes are needed, with the graphene-like material formed directly on the target substrate. This method is known as Laser-Induction/Laser-Scribing, shown schematically in Fig 1.3.

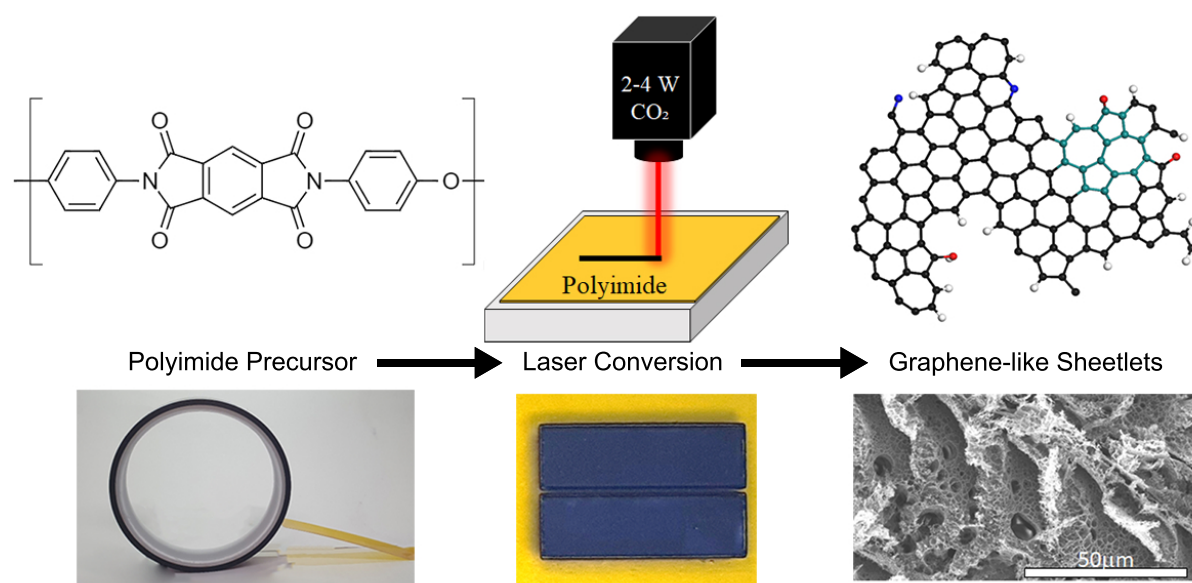


Figure 1.3: Schematic showing the conversion of polyimide into 3D porous, foam of graphene sheetlets. Including, with permission, components from *Dong et al.* [49].

Although the production of graphitic material through laser conversion has been awarded patents as far back as 1972 [50–52], little insight was achieved into the resulting material. Consequently, the accepted initial discovery of LIG, and best understood process, is that of the production of LIG from polyimide. *Tour et al.* used a commercial formulation of polyimide (Kapton), which was converted into graphitic material through a one-step graphitization process of CO₂ laser writing [53]. Polyimide is used in back-end-of-line semiconductor manufacturing due to its high temperature and chemical stability. It can be coated directly onto silicon devices inspiring interest as possible method of integrating graphene-like materials with traditional semiconductor devices. This challenges the more scalable technologies such as rGO and liquid-phase exfoliation, which can produce large volumes of material quickly, but which require numerous process steps to utilise post-synthesis, while LIG is formed *in situ*.

This thesis uses polyimide-based LIG throughout, but alternative feedstock materials have been demonstrated including: treated-wood [54] and -food-products [55]; as-harvested renew-

ables such as cork [28]; chitosan [27], a biopolymer derived from the chitinous shells of prawns, or by using visible laser sources [56]. These alternative material platforms provide a route towards reduced environmental impact and future device biodegradability.

The general formation of LIG can be considered in terms of its formation from polyimide using a CO₂ laser source, as this is the best understood conversion process in literature. The incident laser photons give rise to a photothermal effect, whereby localised heating increases the temperature above that required to break C–O, C=O and C–N bonds [57]. These groups evolve into gaseous species producing high-pressure pockets of gas driving the formation of micro/nano-pores and other structural defects [58].

The remaining carbon groups agglomerate and produce a graphene-like structure facilitated by the high localised temperatures and the presence of the previously formed aromatic rings. The rapidly evolving gaseous components generate a highly porous structure as the gas escapes at high pressure, preventing the formation of homogenous sheets, instead producing a foam-like structure, containing pores and wrinkles visible under SEM imaging [58].

During lasing, the energy transfer is tightly focused due to the narrow beam diameters, the power density ensures that large energy transfers occur more rapidly than relaxation processes. Unlike heating of a sample in a furnace, this results in simultaneous high temperature and high pressure local environments as insufficient time is allowed for volume expansion of the heated material. The vastly different formation conditions have resulted in LIG being extensively characterised in the literature, using techniques typically used for pristine-graphene characterisation, facilitating their direct comparison. These include Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and Raman spectroscopy. Subsequent Molecular Dynamics (MD) simulations have been conducted to investigate the formation processes. These studies are summarised below.

Transmission Electron Microscopy

Structural analysis of LIG via TEM of the resulting graphitic material indicated the presence of pentagon-heptagon pair defects in the graphene layers, i.e. Stone-Wales defects. The presence of the Stone-Wales defects had been shown to result in the bending of the sheets, causing the

formation of wrinkle and cone structures [59]. This allows for the highly three-dimensional structured foams produced to contain hybrid graphene sheetlets [55], see Fig 1.4.

X-ray Photoelectron and Raman Spectroscopy

XPS of the LIG compared to the polyimide indicate increased numbers of sp^2 hybridised C–C bonds and decreased C–N, C–O and C=O bonds, verifying that the outgassing corresponded to the loss of O and N during the laser conversion.

Raman spectroscopy (see section 1.6) revealed the characteristic D, G and sharp 2D peaks indicating the generation of graphitic material, their symmetric shape and large I_{2D}/I_G ratios and distinctly observable defect peaks i.e. D' are characteristic of graphene-like material. The symmetry of the peaks, marks a distinction of the band splitting that would occur in the phonon band structure, corresponding to many layer graphene/graphite. The ratio of the intensities of the D and G peaks showed that graphene had been produced with high crystallinity, and the ratio of the 2D and G peaks suggested that a few-layer graphene had been produced. Similarly, Full-Width-at-Half-Maximum (FWHM) of the 2D peak suggests rotational and/or stacking disorder. Hence, its description as laser-induced graphene (also referred to as laser-scribed carbon, laser-induced graphene-like carbon or laser-induced graphitic carbon in the literature) [59].

Molecular Dynamics Simulation

MD simulations have been used to elucidate the photothermal process arising from the localised heating. *Dong et al.* have simulated the laser conversion of polyimide to LIG through both Canonical Ensemble (NVT) and Isothermal-Isobaric Ensemble (NPT) ensembles [49]. The NVT ensemble allows for pressure change as expected from localised heating of the sample, while the NPT ensemble does not. The canonical ensemble model predicts the formation of LIG-like material suggesting that both the high localised temperature and pressure both contribute in the formation of LIG [49]. It was determined that the process is a combination of heating and pressure effects, as only the NVT ensemble predicts the formation of the expected layered graphene clusters. The determination that pressure is a key factor extends what was assumed as a photothermal process experimentally investigated by *Tour et al.*

Further to the determination that process is pressure dependant, *Dong et al.*'s simulations provide additional insight to the LIG formation process. The MD simulation indicated a process of 6-membered rings opening, 5-member ring and carbon dimer formation with associated small molecule generation (HCN, CO, CO₂, H₂, H₂O, N₂, NH₃). High pressure supresses the conversion of carbon-membered rings into gaseous molecules and promotes dimers and small carbon clusters to bond to opened rings upon catalysis of by N and O containing groups. The model indicates that the 5-membered rings present in the Stone-Wales defects are caused from the breaking of the aromatic rings and not from spontaneous generation; suggesting their unavoidable, intrinsic nature, see fig. 1.4. The MD prediction of Stone-Wales defects and sheet curvature corresponds with the observations of *Tour et al.* [53].

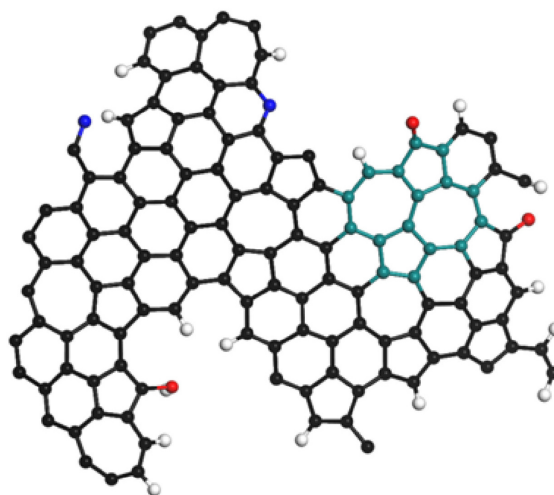


Figure 1.4: Molecular dynamics model of LIG graphene sheetlet, demonstrating Stone-Wales and edge defects. Adapted with permission from *Dong et al.* [49].

The MD simulation also predicted incomplete elimination of nitrogen and oxygen atoms, originating from the polyimide structure, with some remaining at the boundaries. These groups were seen to act as a catalyst during C–C bond formation. This corresponds to the initial testing for materials that could be converted into LIG, whereby, materials required both aromatic rings and imide groups. It is likely that their mediation of bond reformation is what accounts for their requirement in initial substrate. However, their retention in the LIG material allows for their use as adsorption sites like equivalent defects in rGO and CVD-graphene.

Considering together the XPS, Raman, TEM, and MD we have significant insight into the

laser conversion of polyimide into LIG. This process yields a highly-porous, Three Dimensional (3D) foam, comprised of numerous graphene sheetlets, which contain structural and chemical defects. The resulting hybrid structures correspond to a kinetic and not a thermodynamic product; suggesting that the laser-fabricated graphene undergoes rapid cooling after its formation [55].

Further works by *Tour et al.* have focused on several approaches to further modify the resulting LIG material, however, there has been no simulation work to indicate their mechanisms. These include the production of LIG in different gas environments to control wettability [60] and the variation of laser power, while maintaining constant scan speed. The variation of the formation parameters modifies the mechanism and thus controls the quality of the material. In the case of the lasing parameter variation it was observed by XPS that increasing laser power results in increased oxidative defects and increased sheet resistance, which could be mitigated by gaseous environment control [53]. However, the optimisation parameter space is highly complex with numerous inter-related factors preventing meaningful linear optimisations.

The properties of graphene are critically dependent on its structure and any variation results in a pronounced change in its behaviour. Although LIG is graphene-like, it notably contains defects and consequently displays different behaviours including reduced conductivity and enhanced surface area. The nature, extent and distribution of the defects present are associated with the precursor choice and formation conditions, providing a promising platform for optimisation for specific applications.

LIG is unlikely to achieve the ideal material properties of pristine graphene due to unavoidable defects in its formation, e.g. Stone-Wales defects. However, its rapid, *in situ*, formation is an attractive feature for many applications. Similarly, its ease of integration at back-end-of-line would allow for integration of graphene-like materials at low temperature, from precursors compatible with semiconductor manufacturing.

One potential application is for the formation of LIG-based electrodes on flexible substrates, providing a metal-free conductive material for disposable, wearable electronics. To achieve such devices, it would be necessary to have a well-defined set of parameters that can be used to control the properties of the resulting material. For example, a LIG heater device wouldn't need the enhanced surface area, unlike the sensing element of a VOC sensor, but both would

require minimised contact and sheet resistance values. However, the factors that influence these variables are non-intuitive and are often interdependent.

1.4 Gas Sensing Literature Review

In VOC sensing, as in all sensing applications, there are four main factors to consider: Sensitivity, Selectivity, Stability and Noise. The ideal sensor should have a high sensitivity to its target analyte, no response to any other species, no influence from ambient conditions or aging effects, with large responses above any fluctuations due to noise. These are the key performance indicators typical for sensors of all types in literature. A strong, well defined, relationship between responses and the analyte is also necessary. For low power applications, it is also necessary for the sensors to operate under standard ambient conditions i.e. room temperature and be impervious to the effects of water vapour and common gases.

Chemiresistive sensors operate through charge transfer processes between a semiconducting material (or material with a low charge carrier density) and an analyte species. The charge transfer produces a change in conductivity at the surface. This assumes a direct interaction. However the interaction process can also be indirectly mediated by another surface species or decorating material. This is especially common for oxygen mediated processes on semiconductor MOX sensing layers, at elevated temperature, as will be discussed in section 1.4.3. As this can also occur for particle decorations on any sensing material, the underlying concepts will be discussed briefly in terms of the oxygen adsorption onto an arbitrary surface.

Due to its atmospheric abundance, the role of oxygen adsorption onto the sensing layer should be considered. Oxygen molecules adsorb onto the sensing layer and, typically, withdraw electron density from the surface to yield activated charged oxygen species (O_2^- , O^- , O^{2-}), depending on the temperature. This electron withdrawal results in the initial modification of the charge carrier concentration, and thus, the resistance. Activated oxygen species can then react/interact with analyte gases, either experiencing charge donation/withdrawal or acting as reducing agents. If they reduce another species, the resulting charge exchange and desorption results in the return of the withdrawn electron from the supporting surface, reversing the oxygen species initial electron withdrawal, and the associated conductivity and resistance changes.

LIG could be employed in two distinct ways for VOC sensing, either as the active sensing element (see section 1.4.2) or as a resource efficient, high surface area supporting electrode (see section 1.4.3). The relevant discussion for both morphologies will be considered separately. However, in both instances similar sensitisation enhancements are demonstrated by decoration of the active material with additional nanomaterials. This underlying process is discussed first.

1.4.1 Sensitisation

Nanoparticle sensitisation of sensors follow two typical methods, spill-over and Fermi-level control. These general processes hold regardless of the nature of the underlying material (e.g., graphene or semiconductor MOX). In most cases pristine, unmodified, sensing materials typically have poor selectivity, poor stability and are easily influenced by water vapour. But catalytic materials and/or mixtures of semiconducting MOXs can be used to enhance their sensing performance.

Chemiresistive sensing can be discussed in terms of two coexisting, although not independent, processes: reception and transduction. Reception refers to the uptake of analytes and reactants (both adsorption and preparation of surface reactants e.g. catalysis of water into surface hydroxyl groups), while transduction refers to the how this interaction becomes a measurable electrical response. While not fully separable, these processes allow for clear optimisation routes and discussion of different functionalisation routes together. Typically, the reception is ascribed to surface properties such as defects, functional groups and adsorption sites whilst the transduction is described in terms of carrier depletion layers, charge barriers and reaction profiles. The effects on the reception and transduction are commonly referred to in the form of spill-over and Fermi-level control mechanisms [61].

Spill-over

The spill-over mechanism, also known as chemical sensitisation, occurs when a decorating material allows for facile adsorption of a target analyte onto the surface, after which it migrates to the sensing material. For chemical defects, or functional groups, this can be a high energy adsorption site, or a specific interaction, while for metal catalysts it is typically the adsorption

onto the metal adsorption sites. This ensures an efficient supply of reactants to support the reaction mechanism of the undoped/undecorated support material, without modification of the reaction [62]. This is a catalysation of the reception process. For instance, the presence of a noble metal could allow for greater adsorption and spill-over of oxygen species, thus increasing the depletion/accumulation layer, and so the transduction process is enhanced indirectly, but through the same underlying mechanism.

Beyond enhancing sensor specificity or response magnitude, this can also allow for reduction of the sensor operating temperature. This is typically facilitated by better adhesion or dissociation kinetics on the decorating metal surface/functional group. Typical examples of this include the enhanced adsorption of oxygen species on Au NP cluster decorating SnO₂ followed by their transfer to the SnO₂ surface, where they become ionised, thus withdrawing electrons from the SnO₂. The adsorbed oxygen species can then react with CO, returning the withdrawn electrons. This increases the response signal, by amplifying the initially withdrawn electrons and increasing the surface oxygen concentration for reaction with the CO analyte [63,64]. Spill-over effects can be extended beyond the typical oxygen adsorption enhancement and migration, to take advantage of known material-analyte adsorption pairs to enhance the reception of analytes.

Fermi-Level Control

In contrast to the spill-over mechanism, which enhances the underlying mechanism, the Fermi-level control mechanism instead modifies the surface and can alter the mechanism or even open alternative reaction routes. Decorated metal oxides can interact electrically with the supporting material, acting as electron donor/acceptors, inducing Fermi-level pinning, and resulting conductivity change. The coupling of the decorating material and the support results in any charge carrier redistribution in the decoration layer, propagating into the semiconductor MOX system, affecting its conductivity.

Ag decoration on SnO₂ is a good example. Ag is known to easily oxidise. When deposited onto metal oxides it typically exists as a redox couple (Ag^+/Ag^0) when oxidised in air. Consequently, the SnO₂ Fermi-level is pinned to the Ag^+/Ag^0 electrode potential, which produces an electron depletion region. However, reducing gases can easily reduce AgO back to metallic Ag.

This results in the release of the trapped electrons and the reversal of the Fermi-level pinning to the work function of the metallic silver, which instead increases the surface conductivity [61, 65]. This provides a different reaction scheme than would be possible on the undoped/unmodified MOX and is considered a change to the transduction.

1.4.2 Laser-Induced Graphene-like Carbon as a Sensing Element

Significant work has been dedicated towards the development of graphene-based chemiresistive sensors, with the first demonstration being achieved this year for the detection of NO_x [66]. Given that LIG is composed of numerous graphene-sheetlets, it could in future be used as a facile production route for a graphene-like chemiresistive sensing element at a lower resource cost than current chemiresistive sensors.

As has already been stated, graphene has long been lauded by its proponents as having an incredibly high surface/volume ratio, low electrical noise and high electrical conductivity [29]. However, this is not exactly correct, rather than having a high conductivity, pristine graphene monolayers have a high carrier mobility, but a low carrier concentration, therefore it is often described as a semimetal or a zero bandgap semiconductor. Its conductivity depends critically on the number of carriers present and their modification results in an observable change in the macroscopic variable resistance. Similarly, the high surface-area/volume ratio of graphene results in a large surface area/unit mass of $\sim 2600 \text{ m}^2/\text{g}$ presenting a large number of available sites for adsorption and detection [67].

In ground breaking work, *Schedin et al.* devised a pristine graphene sensor capable of detecting individual gas molecules adsorbing onto the surface modifying the conductivity through electron donation/withdrawal [38, 68]. This set out the potential for very sensitive graphene-based gas sensors. However, the challenge is the poor selectivity of these sensors. They would only be able to determine the presence of gas molecules and their electron donation/withdrawing nature. This allows for the use of graphene in sensing in a number of different ways including: optical fibres coatings [69]; interferometric suspensions [70]; oscillator cell coatings [71, 72]; sensing elements below microporous selective membranes [73]; impedance based graphene sensors [74] and chemiresistive methods which is the most common method in the literature.

The sensitivity to electron donation/withdrawal, combined with the significant surface area of graphene is highly suggestive of viable chemiresistive VOC sensors. The proliferation of adsorption sites allows for numerous donation/withdrawal interactions to occur simultaneously, increasing the magnitude of charge carrier modification and consequently the response. It shows there are two main controlling factors: the electron transfer mechanism and the adsorption site availability.

The poor selectivity of pristine graphene and the manufacturing bottleneck of mechanical exfoliation led to the use of two main branches of the material; chemical vapour deposition grown graphene and rGO. CVD-graphene and rGO both contain higher defect concentrations than pristine graphene. These defects manifest as vacancies, deviations from the ideal crystal structure, and most notably the inclusion of non-carbon functional groups (e.g. hydroxyl, carboxyl and epoxide). These groups are normally electron withdrawing and result in net p-doping of the main body of the sheet [75]. They are also energetically favourable sites for adsorption of molecules and sites of higher reactivity relative to the stable hexagonal carbon lattice.

Work by *Choi et al.* [76], who fabricated NO₂ sensors on multi-layer graphene indicated good responses but highlighted a further concern for the use of graphene sensing. There was a poor desorption of the NO₂ without increasing the temperature of the device, which should be considered for all typically high temperature sensors. This, combined with the lack of sensitivity, indicates the need for modifications away from pristine graphene material if room temperature gas sensors are to be achieved. Approaches towards achieving these room temperature devices fall into two distinct categories; defect modification and the introduction of external functionalisation groups (used here to mean functional group modification and introduction of external materials).

The sensing mechanism of pristine graphene is relatively intuitive, as shown in Figure 1.5. The electron donating (e.g. NH₃) or withdrawing (e.g. NO₂) group adsorbs onto the graphene surface at an energetically favourable site. Donation of electrons results in the recombination with holes in the p-doped graphene, increasing resistance. Withdrawal of electrons results in creation of additional holes, decreasing resistance. The extent of the electron exchange depends on adsorption site, distance from the surface and nature of the adsorbate gas.

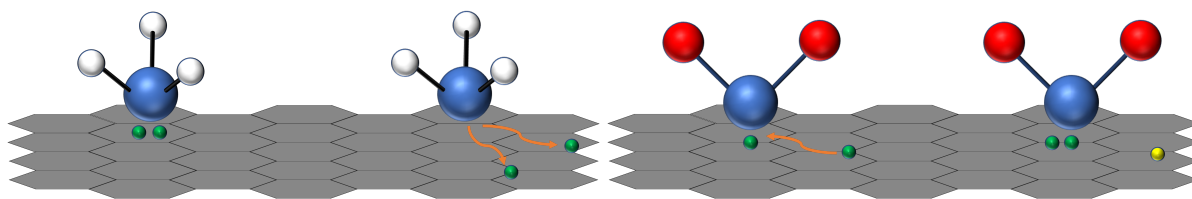


Figure 1.5: (Left) Electron donating group (NH_3) physisorbed on pristine graphene, (Right) Electron withdrawing group (NO_2) physisorbed on pristine graphene. Nitrogen marked in blue, hydrogen marked in white, oxygen marked in red, electrons marked in green, and holes marked in yellow.

The chemical stability of the graphene sheet results in poor selectivity to different adsorbate gases. The introduction of defect sites, as seen in CVD-G or rGO, results in more energetically favourable sites for specific molecules to adhere, as the functional groups can interact directly with adsorbed molecules increasing the extent of the electron exchange. Figure 1.6. shows an example of Density Functional Theory (DFT) investigations by *Mattson et al.* [77] of rGO adsorption sites for NH_3 and the resulting reactivity. The inclusion of defects in the graphene structure facilitates their modification into other functional groups more easily than direct chemical functionalisation of pristine graphene.

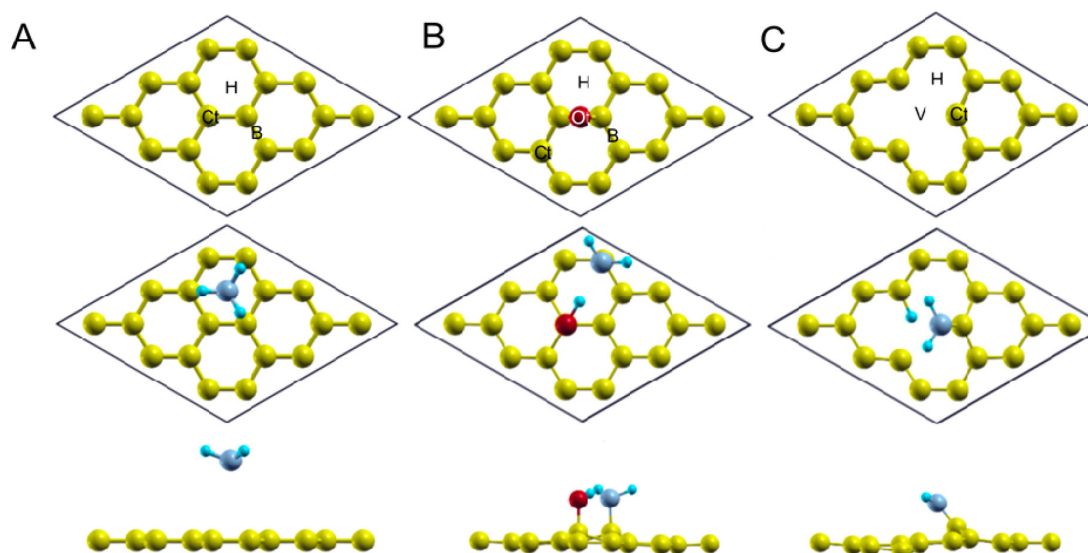


Figure 1.6: a) Physisorption of ammonia on pristine graphene, b) Epoxide defect site results in sensitisation to ammonia promoting chemisorption, c) Vacancy defect site promoting chemisorption of ammonia. Adapted with permission from *Mattson et al.* [77].

Functional group modifications can be achieved in several different ways, including post-synthesis modification, altering synthesis conditions and modifying the production pathway. *Shekriev et al.* grew arrays of graphene nanoribbons by CVD while maintaining a temperature

gradient across the growth metallic surface [78]. Due to the difference in the growth conditions, each element of the array contained different distributions of defects. The array was then used to fingerprint different gas responses through the response vector. The response vectors of various gases were used to train a machine learning model to recognise these gas environments. These sensors achieved accurate discrimination of different alcohols indicating that functional group modification allows for enhancement of selectivity.

The selection of graphene as a sensing material is heavily influenced by its high surface area/volume ratio and associated high number of adsorption sites. However, the potential of non-analyte gases to be adsorbed must be controlled, such as water vapour from humidity. These molecules, at best, can occupy sites preventing their use by analyte gases or at worst result in an electron exchange resulting in poor selectivity. Functional group modification of rGO, converting hydroxyl groups into amines has resulted in the control of the wettability of the surface, preventing water vapour adsorption [71].

More extensive functional group modifications have also been attempted, e.g. sulfonated rGO hydrogels [79]. This used NaHSO_3 to reduce Graphene Oxide (GO) and instead of leaving oxygen groups at the edge of the resulting flakes, instead networks of interconnected sulfated graphene-like flakes were produced. These sulfur groups (HSO_2^-) are electron-rich and are selective towards electron withdrawing groups, relative to standard rGO defects. An additional benefit of the reducing agent used is the 3D porous structure, enhancing the number of surface sites available in a given areal footprint. This increases the number of active sites for adsorption events to occur and would consequently increase the observable response and sensitivity of the sensor.

Other methodologies have been explored to enhance the available surface area without targeting a modification of the functional groups. These include using other carbon allotropes such as carbon nanotubes in conjunction with rGO to produce porous distributions [80], sacrificial holey Ni used as growth scaffolds for CVD-G [81] and the use of hybrid graphene-Metal-Organic Frameworks (MOFs) [82]. G-MOF hybrid structures demonstrated enhanced surface areas $\sim 10\times$ due to the resulting mesoporous foam structure, resulting in enhanced responses to the analyte gas (chloroform) [82]. The introduction of the metal groups and ligands also provide

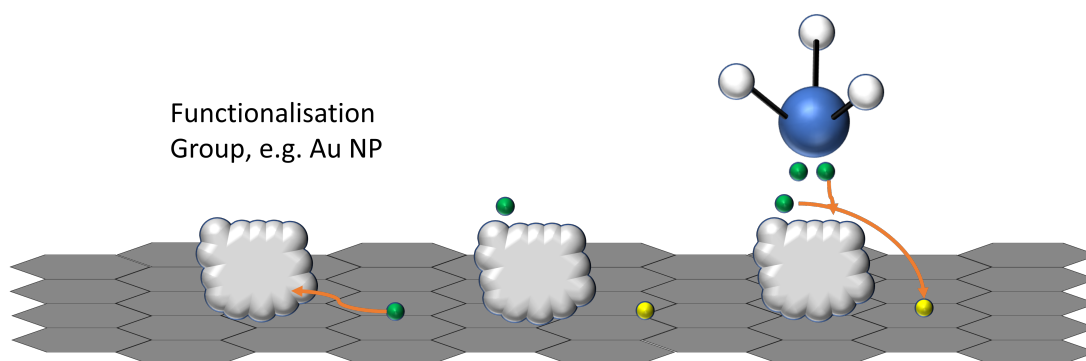


Figure 1.7: Electron exchange interactions between graphene, external functionalisation additions and analyte gases (ammonia). Nitrogen marked in blue, hydrogen marked in white, electrons marked in green, and holes marked in yellow.

attract adsorption and coordination sites for the analyte promoting further selectivity beyond what could be explained by the surface area enhancement.

The use of external functionalising materials is distinct from modifying already present functional groups. The chemical nature of the underlying graphitic material remains unchanged. However, the introduction of metal or metal oxide groups, due to their differing electronic structure, results in a redistribution of electrons to align Fermi levels and consequently the doping of the graphene. In most cases, such as metal NPs, their distribution along a graphene surface results in the transfer of electrons from the graphene into the NPs, due to its larger work function. Similar interactions occur with commonly used metal oxide semiconductors such as SnO_2 and ZnO . Due to the redistribution of charges, the functionalisation materials become energetically favourable sites for adsorption and interaction.

One possible interaction type with an electron donating group is shown in Figure 1.7. The distributed NPs result in electron withdrawal from the p-doped graphene sheet, decreasing resistance. When electron donation occurs due to adsorption of the electron donating group, the electrons redistribute into the graphene sheet to ensure the Fermi-levels align, increasing resistance. This process is similar to that of pristine and functional group modified graphene.

As already outlined in section 1.4, alternative reaction pathways are also possible with NP decoration on graphene. The catalytically enhanced oxidation process facilitated by metal NP decoration is shown in Figure 1.8. In this case, oxygen groups are attracted to the high electron concentration of the functionalisation groups and acts as an electron withdrawing group, decreasing resistance of the underlying graphene (net p-type from adsorbates, e.g. H_2O).

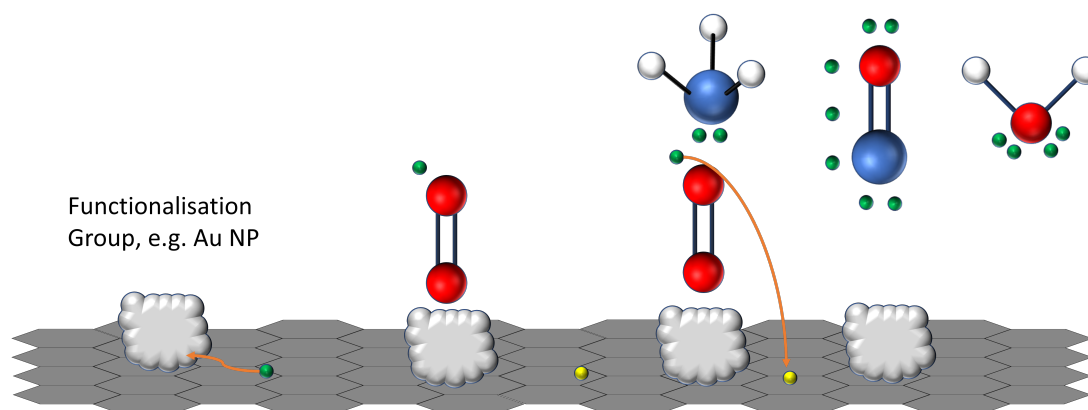


Figure 1.8: Catalytically enhanced oxidation reaction occurring at external functionalisation addition. Nitrogen marked in blue, hydrogen marked in white, oxygen marked in red, electrons marked in green, holes marked in yellow.

Depending on the temperature of the process and the surface to which the oxygen group is adsorbed, different anions can be formed (O_2^- , O^- , O^{2-}).

When the analyte gases adsorb onto the surface, they are oxidised by the oxygen ions. The withdrawn electrons are then returned to the graphene sheet, increasing resistance. The choice of the material added to the graphene sheet determines the selectivity towards different gases, their adsorption and facilitates the production of oxygen ions. This can increase the selectivity of the sensor beyond that of unfunctionalized graphene. As will be discussed in section 1.4.3, early VOC sensors were produced using this mechanism for varying the resistance of thin films of semiconductor materials, for example ZnO [83] and Pt-WO thin films [84]. However, these devices required high temperature to function ($> 400^\circ\text{C}$); unsuitable for room temperature applications.

These early investigations have inspired numerous works that have employed this sensing on a graphene support using different NPs to enhance selectivity towards their respective analyte gases, e.g. Pd- H_2 , Ag- CH_4 , $\text{SnO}_2/\text{TIO}_2$ - NH_3 and ZnO-formaldehyde [85–87]. The specific reactions that occur depend on the behaviour of the exact metal/metal oxide NPs and their respective interactions with graphene. The sensing mechanism of most of these functionalisation NPs is a combination of electron density transfer to/from the surface, either directly or else indirectly mediated by adsorbed oxygen species. Beyond facilitating the reduction of operating temperature for the oxidation process, NP decoration also increases the number of reaction sites for a given mass loading.

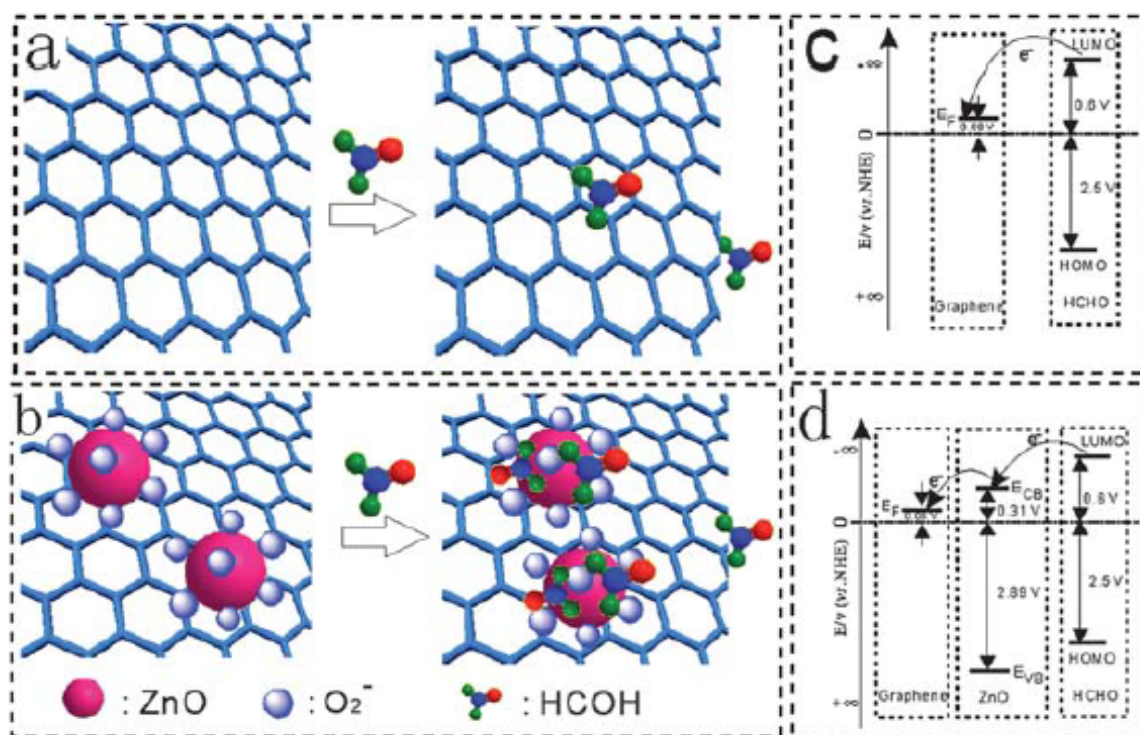


Figure 1.9: a) Adsorption behaviour of formaldehyde on graphene, b) Adsorption behaviour of formaldehyde on ZnO NPs, c). Electron transfer process between formaldehyde and graphene, d). Electron transfer process between formaldehyde, ZnO NPs and graphene. Adapted with permission from *Huang et al. 2012* [87].

Expanding on the example of ZnO for formaldehyde detection, shown in Fig. 1.9, that prior to the functionalisation, the donation of electrons by the formaldehyde was energetically favourable, however the introduction of the NPs create an alternative transfer pathway. Further, the introduction of the NPs also results in the formation of oxygen anions, which as previously mentioned, can oxidise the analyte gases resulting in an electron exchange occurring.

Of the methods used to enhance graphene as a VOC, sensor the most promising of those discussed are the production of 3D mesoporous networks of graphitic material, the intentional production of defects in the graphene structure to produce high energy sites for interactions and the use of externally fabricated NPs to further enhance selectivity.

LIG is a particularly interesting candidate for VOC sensing, due to its highly 3D porous structure, comprised of sheetlets of few-layer graphene, as has already been discussed in section 1.3.1. These small-scale graphene-like structures combine with its known defects, e.g., Stone-Wales, and functional groups arising from incomplete evolution of small chemical groups to

yield a highly porous, conductive 3D foam material. As was discussed for both rGO and CVD-G, the functional groups can act as adsorption sites, allowing some native specificity and reactivity for gas sensing. This would allow for the direct-write production of material similar to that discussed for graphene-MOF hybrids and carbon-allotrope mixtures to enhance the available surface area as can be seen in Figure 1.10.

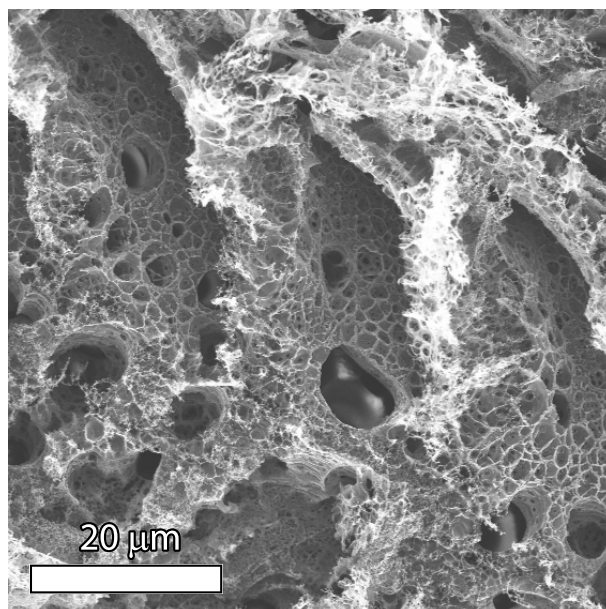


Figure 1.10: Scanning electron micrograph of porous foam-like LIG micro/nanostructure.

The LIG discussed here, primarily focuses on polyimide-based LIG, due to its prevalence in the literature as the primary precursor for LIG production. Further, polyimide is commonly used in semiconductor manufacturing due to its high temperature and chemical stability, which provides a valuable route for integration of LIG functionalisation at the back end-of-line. However, as has been noted in section 1.3.1, LIG has been demonstrated on many different substrates and using various laser source to yield graphitic material, providing future, lower resource cost fabrication routes.

1.4.3 Laser-Induced Graphene-like Carbon as a Supporting Electrode for Metal Oxide NPs

LIG can also be employed as a supporting electrode for separately fabricated sensitising materials. The underlying mechanism of this variety of chemiresistive sensors are similar to those already discussed, with graphene as the active material see section 1.4.2. However, as the sensing in this

case is mediated by the semiconductor particle network, which introduces additional complexity it is also necessary to consider that literature.

Chemiresistive semiconductor MOX VOC sensors have been demonstrated using various Semiconducting Metal Oxides (SMOXs), both n-type (SnO_2 , ZnO , TiO_2 , In_2O_3 and WO_3) and p-type (Co_3O_4 , CuO , Cr_2O_3 and NiO) [84, 88–96], as pristine materials; in combination with other semiconductor MOX; and with doping/surface decoration with metals/metal oxides. However, the underlying mechanisms, modes of operation and chemical reactions are not conclusively established in the literature. The process depends on the specific metal oxide used (p-/n-type, surface chemistry), sensing layer morphology (particle size, surface/volume ratio) and decorating material (surface chemistry, electrical interaction). These contributions, and their combinations, have allowed for a great number of sensors to be developed for various VOC analytes.

As outlined in section 1.4.1 for a general chemiresistive sensor, the operational mechanism of any semiconductor MOX VOC chemiresistive sensor comprises two parts: reception and transduction. The former refers to the reaction of analyte gases with the surface and the latter refers to the transformation of this interaction into a measurable electrical signal. In bulk sensors, the reception is typically caused by the surface of the particles and the transduction is through the microstructure of coagulating particles, as the resistance of the polycrystalline structure. To build an understanding of the underlying mechanism it is necessary to introduce their contributions incrementally.

For undoped/undecorated semiconductor MOX sensing layers, the presence of atmospheric oxygen allows for the adsorption or ionosorption, depending on the device temperature, of oxygen species onto the surface of the semiconductor MOX. The adsorbed oxygen species act as electron-withdrawing groups and result in the formation of a surface-depleted space charge layer. This results in the formation of an electron depletion layer (or hole accumulation layer in the case of p-type). The extent of the layer is controlled by the concentration of oxygen at the surface, and the Debye length (L_D) of the semiconductor MOX, to screen the electron withdrawal.

Correspondingly, the surface resistance differs from that of the bulk core, increasing/decreasing the resistance n-/p-type respectively. This is the key underlying mechanism for most semiconductor MOX chemiresistive VOC sensors. Subsequently, analyte gases, typically reducing

gases (electron donating), can interact with the adsorbed oxygen species, relaxing the surface charge effects and reducing the depletion/accumulation layer depth. The nature of the interaction between the adsorbed oxygen and the target analyte defines the reception of the sensor [97].

p-/n-type Semiconducting Metal Oxide

Considering a model system of a single grain of semiconducting material electrically contacted at each end. For either p-/n-type, the conduction can be considered in terms of its components as shown in fig. 1.11, whereby the contact resistance, skin conduction and bulk conduction components can be disaggregated into individual conduction elements. As with any parallel resistance paths the lower resistance pathway determines the system resistance.

In n-type systems, the lowest resistance path is through the central core region, which requires the charge path to traverse through the high-resistance skin, through the low-resistance core and again through the skin. For the p-type system, the resistance favours the lower resistance skin pathway, with minimal transfer through the higher resistance core. The conductivity changes used for chemiresistive sensing arise from the variation of the thickness of these accumulation/depletion layers, as they open/restrict conduction channels.

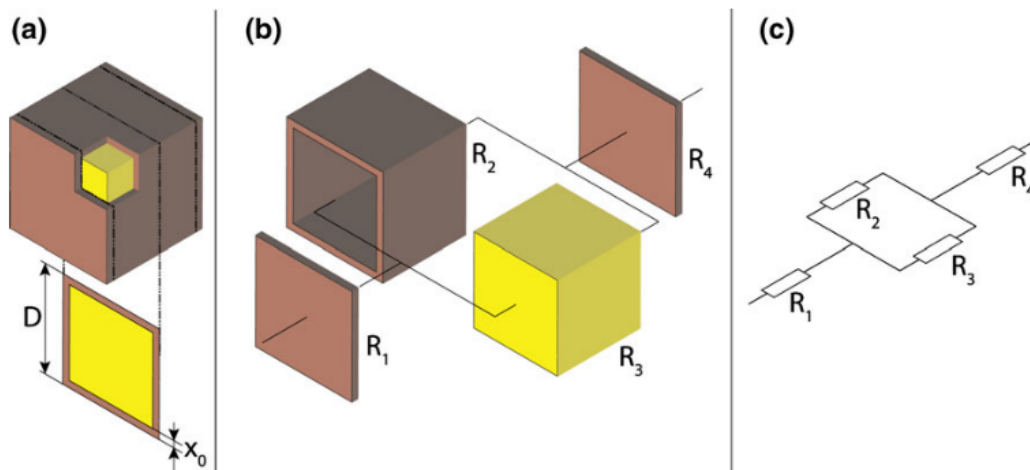


Figure 1.11: Simplified model of a metal oxide grain used for calculation of the grain resistance. (a) the cubic grain model; (b) sketch of the electrical connection between the different grain parts; (c) the corresponding DC equivalent circuit of the grain. Reproduced with permission from Barsan *et al.* 2010 [98].

This single-grain model can be extended to a multi-grain model, more like what would be seen for nanoparticle network systems, see figure 1.12. In this view, neglecting grain boundary

effects and assuming a high degree of depletion/accumulation, n-type conduction comprises sequential conductive cores joined by resistive regions, arising from the depletion layer. For p-type conduction, two parallel paths contribute to the conduction: the more resistive core and the more conductive accumulation skin layer.

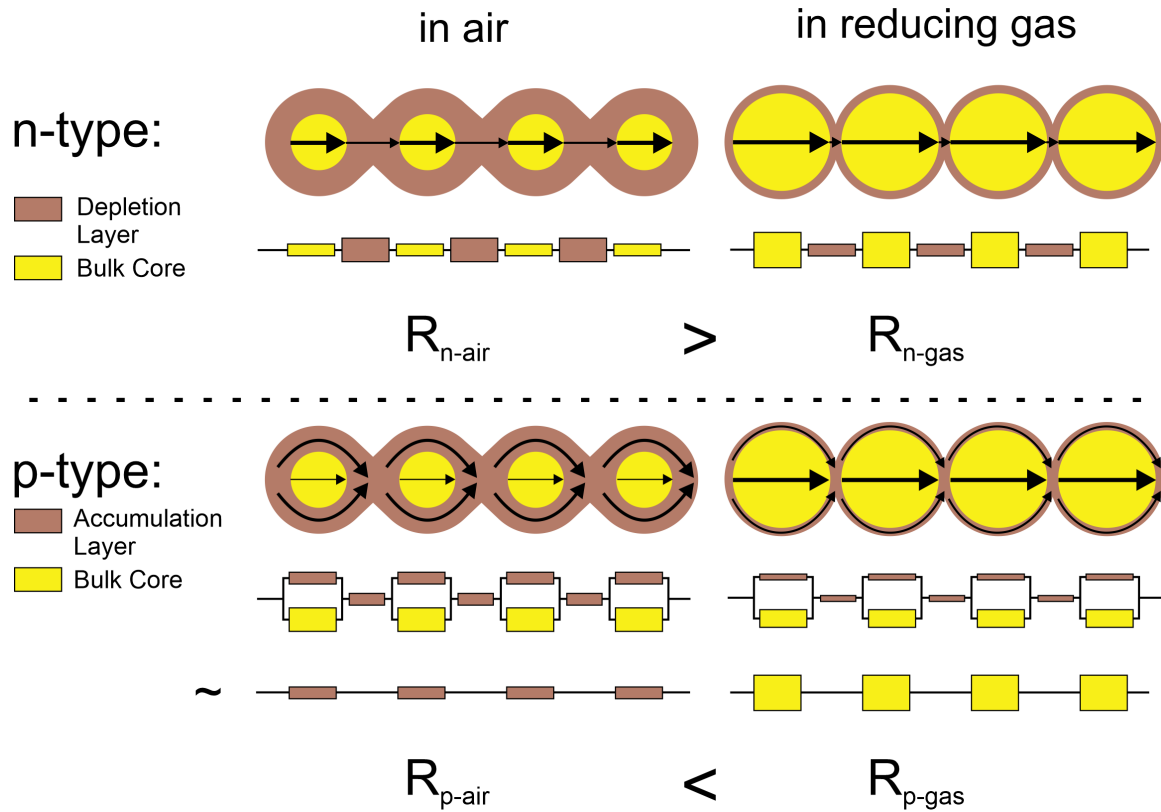


Figure 1.12: Schematic of (top) n-type granular semiconductor MOX particle array conduction mode in air and reducing gas and (bottom) p-type granular semiconductor MOX particle array conduction mode in air and reducing gas.

The effects of reducing gases interacting with electron-withdrawing species and returning electron density can also be considered under this framework. For n-type, there is a reduction in the depletion layer thickness. This reduces the resistance in two key ways: the widening of the conductive core (traditional resistivity cross-section argument) and the reduced distance to be travelled through the depletion layer. For p-type networks the increase in resistance is due to the relaxing of the accumulation layer, returning towards the conductivity of the core.

Particle Miniaturisation

In n-type semiconductor MOX, there is a well-established sensitivity response on the particle size, especially for well-connected, sintered devices, as shown in figure 1.13. The figure shows

a continuum of particle diameters, joined together into a linear array. The depletion layer that would be experienced due to oxygen adsorption is shown relative to the particle size in each instance. This gives rise to four regimes, corresponding to neck diameter relative to the Debye length: wide necks ($D \gg 2L_D$), necks ($D > 2L_D$), depletion layer boundaries ($D < 2L_D$) and complete depletion (either $D \ll 2L_D$, or $D < 2L_D$, with high modulation) [97].

The wide neck regime experiences minimal modification by gas exposure, as the effective width of the necks remains unchanged. The neck regime corresponds to the initial improvement of sensing of particle networks over thin film structures. This enhancement arises from the series nature of the conduction network and “weak link” necks that can be effectively thinned to produce only a narrow channel of the remaining conductive core.

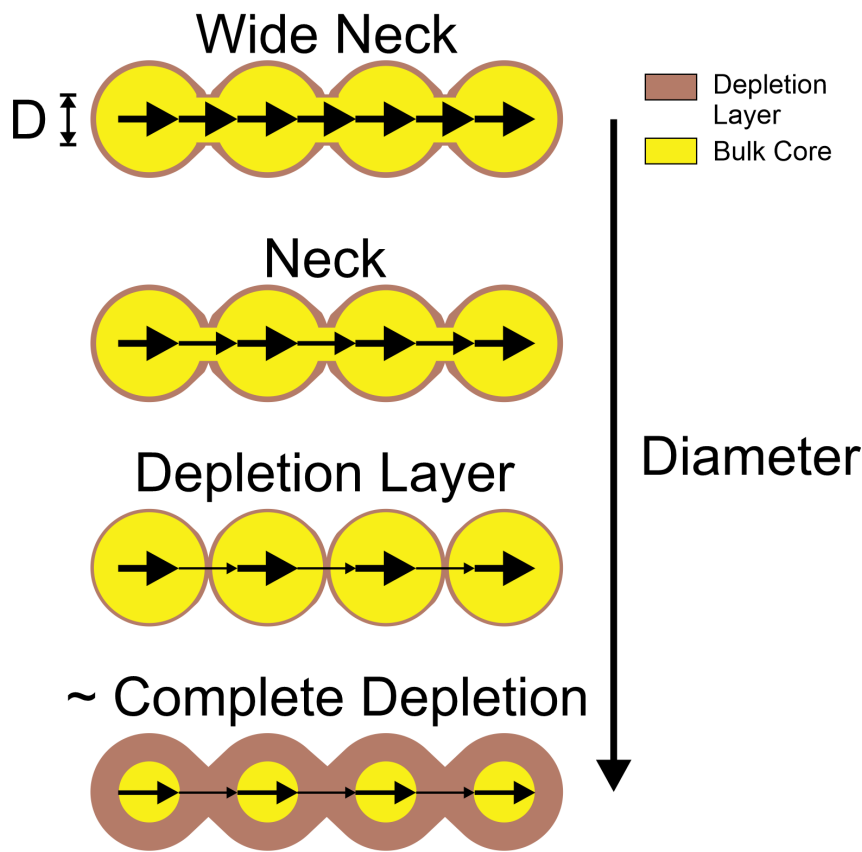


Figure 1.13: n-type granular semiconductor MOX particle array conduction mechanism dependence on particle diameter.

Even smaller particles show a further enhancement and correspond to the breakdown of the interconnection between the core regions. This replaces the traditional resistivity and cross-section argument with serially connected high-resistance electron-depleted regions increasing

the resistivity. Decreasing the particle diameter, not only allows for this behaviour to dominate when the neck diameter decreases below the Debye length, but also requires more particles to bridge the same distance; both the effect of individual and number of boundaries are increased. Finally, decreasing the particle dimension further allows for the complete depletion of charge carriers, increasing the resistance of the device [99].

For particles that experience complete, or effectively complete depletion layers, they no longer have two parallel conduction paths; one through the resistive skin and one through the conductive core. Instead, there are islands of low-resistance cores with high-resistance regions between them that must be traversed for conduction to occur. This amplifies the effect of miniaturisation greatly, as all charge carriers are influenced by any perturbation (such as the return of electron density upon the interaction of adsorbed oxygen with reducing gases) that subsequently modifies the depletion layer, as there is no alternative conduction route.

Further information about the influence of particle size in p-type systems, decorating materials and particle morphology on sensing performance for semiconductor MOX systems is described in Appendix A. The additional discussion focuses on p-/n-type specific optimisation routes, discussion of known particle decoration enhancement mechanisms and a summary of benefits and limitations of different particle morphology for VOC sensing applications.

1.5 Contact Resistance

Since its discovery by *Novoselov et al* [100], graphene has shown great promise as a current carrier or for high frequency field effect transistors due to its high-mobility. Similarly there has been significant interest in graphene for use as a sensing element due to the low charge carrier density. However, if graphene-based technologies are to fulfil this potential and fulfil their potential as a candidate for continuing Moore's law in the miniaturisation of transistors, they first need to become comparable with state-of-the-art devices. This would require that their main limitation, parasitic resistance contributions, are mitigated. Chief amongst these is the contact resistance, described as a fundamental limiting factor in GFET devices [101].

Due to the critical importance of mitigating contact resistance effects on LIG VOC sensors this work has developed facile, direct-write routes to form low-resistance contacts to LIG through

laser-graphitization of thin polyimide layers deposited on ultra-thin metal films. Additional information about the challenges associated with fabricating reliable electrical contacts to graphene are discussed in detail in Appendix B.

1.6 Raman Spectroscopy Theory

Raman spectroscopy is possibly the most valuable method for rapid, quantitative assessment of the quality of graphene and related materials (including LIG) [102]. Appendix C provides a concise overview of Raman Spectroscopy Theory for graphene in terms of point group theory informed by real space and band structure considerations. Table 1.1 shows allowed Raman active processes and their sources, based on group theory considerations of phonon vibrations in terms of in-plane Longitudinal Optical (iLO) and in-plane Transverse Optical (iTO) modes.

Table 1.1: Raman peaks and associated phonons in monolayer graphene.

Peak name	Energy (cm^{-1})	Phonons	Process
D	1350	iTO near K	Defect Assisted
G	1580	iLO and iTO near Γ	First Order
2D	2700	iTO near K	Double Resonance
D'	1600	iLO near K	Defect Assisted
D+D'	2950	iTO near K and iLO near K	Defect Assisted

A Time-Dependent Perturbation Theory (TDPT) model predicts Lorentzian peaks with FWHM of 24 cm^{-1} [103]. It further predicts peak behaviours such as the G peak FWHM only depending on the phonon band structure and the intensity following only a small dependency on the excitation frequency and phonon lifetime. The modelling also predicts the behaviour of various peaks due to increasing defect concentration. Defect concentration can be considered through the mean distance between defects L_D . At low defect concentrations, defect-assisted Raman modes are seen to increase in intensity, corresponding to an increase in their probability of occurrence [104, 105]. The most obvious of these peaks is the D peak. For consistency between apparatus, the intensity of the D peak is normalised by the intensity of the G peak, the resulting value at low defect concentration scales as: $I_D/I_G = 1/L_D^2$. As the number of defects increase so does the intensity of the D peak. However, at high concentrations these effects are seen to reverse with a steep decrease in intensity. This change in behaviour is due to the increase of electronic decay widths due to the presence of the defects. The presence of the defects also results in a relaxation of symmetry requirements in the Double Resonance (DR) process allowing more frequencies to take part, increasing the FWHM of all DR associated processes. This occurs regardless of the necessity of defects for the DR process. In non-defect

assisted processes, they do not experience the increasing intensity effect with concentration, instead they are only dependent on the decay widths of the electronic states. Further, rotational and stacking disorder result in the broadening of the FWHM broadening of the 2D peak [102].

Notably the differing evolution of double resonant and defect assisted peaks with increasing defect concentration can thus be used to estimate the defect concentration. The intensity of peaks that don't depend on the presence of defects to be present, i.e. G and 2D peaks, remain essentially constant at low defect concentration, while D and D' peaks increase in intensity. At higher defect concentration the D peak intensity begins to reduce while the D' peak remains constant. This allows for the use of I_D/I_G peak ratios to determine the extent of defects. When defect concentration is high and the D peak intensity begins to reduce, the intensity of the 2D peak should be considered. As high defect concentrations, the 2D peak intensity begins to decrease due to the high levels of damage to the graphene structure. This has been well established and discussed in the literature [106]. This is important in the determination of samples such as reduced graphene oxide which is graphene that has been produced from a highly defective precursor.

The coupling of TDPT, real space and group theory have allowed for a good theoretical understanding of the Raman spectra of graphene-based samples showing that peaks that are present can indicate the presence of the defects, and their intensities define their concentration. The peak shapes can indicate the presence of additional layers of graphene and the altering of the electronic and phonon dispersion bands. Additional factors such as dopants and strain can then be considered based on these effects on these band structures and electron decay widths. For example, strain results in a breakdown in the degeneracy of the iTO and iLO phonons at the Γ point resulting in a peak splitting of the G Peak.

Based on this understanding, a few characteristic measurements have been carried out on known graphene-based samples to produce experimental standards to which unknown graphitic spectra can be held. The most significant of these correspond to the behaviour of the 2D peak in response to layer number. As described through group theory, the 2D peak for Bilayer Graphene (BG) and Trilayer Graphene (TG) are made of numerous peaks and as such can be challenging to fit. By studying known layered films the ratio of G and 2D peaks (I_G/I_{2D}) and

FWHM of the 2D peaks fit with a single Lorentzian have been catalogued for few-layer graphene samples as presented in Table 1.2. Similarly the position of the 2D peak has been seen to vary depending on layer number, ranging from 2685 cm^{-1} for a monolayer to 2717 cm^{-1} at ten layers, as recorded with a 514.5 nm laser, due to the dispersion in the phonon band structure [107]. These observations correspond with the previously outlined theory, however additional features have been observed such as an unpredicted broadening of the G peak with increasing defect concentration despite being a first order process. This occurs, not due to the variation in the electronic decay width, but instead is caused by an increase in quantum mechanical confinement brought about by the high defect concentration [108].

Table 1.2: Empirical parameters to determine graphene layer numbers in few layer graphene using single Lorentzian lineshapes [107, 109–111].

Parameter	Monolayer	Bilayer	Trilayer	Tetralyaer
I_{2D}/I_G	> 2	0.9-1.4	0.8	0.7
2D FWHM (cm^{-1})	27.5	62	71	72

So, if the structure of polyimide based LIG is considered it is seen to be a hexagon/pentagon-heptagon polycrystalline material, that will contain additional defects due to the incomplete evolution of functional group of polyimide. Both features can separately be considered to increase the concentration of impurities resulting in prominent defect assisted peaks and a noticeable broadening of DR peaks. The hybrid crystallinity produces an additional effect over that of being a point defect. Due to their deviation from the ordered 6-membered ring structure they result in a bending of the sheet as previously described. Sheet bending in graphene has been observed, in the transition between stage one and two graphene intercalated compounds, to produce an increase in the D peak intensity [112]. Additionally, due to the mechanical damage caused by the high-pressure evolving gases the presence of non-chemical defects is also expected to increase the defect peak concentration. As such these features indicate that LIG should have a high intensity D peak beyond that expected due to just the concentration of defects. The highly porous foam structure also makes the investigation of the number of layers of graphene challenging for techniques such as atomic force microscopy, instead this can be investigated from the 2D peak as outlined. As defects concentration and layer thickness are the critical defining features, and due to the well understood formation process and atomic structure of LIG, it is seen that Raman

spectroscopy is a sufficient technique to encapsulate the critical chemical features of LIG.

As has been shown in the discussion above, Raman analysis of graphene and graphene-like materials is rapidly becoming a mature field with increasing levels of detail about the structure becoming extractable from the Raman spectra. The first level of additional extractable information is in terms of the extent of defects present in the graphene material. Further information can be extracted in terms of peak shifting due to doping or band splitting due to multiple layers. However, further analysis of the graphene peaks has allowed for additional information to be extracted. Notably this occurs from the differing dependences of the D and D' peak on defect concentration. Both D and D' peaks require activation by defects and can be modelled as $I_D \sim A_d n_d$, $I'_D \sim B_d n_d$ so $I_D/I'_D \sim A_D/B_D$ in the low defect concentration stage. By controlled modification of graphene it is observed, that depending on the nature of the damage/defects present in the graphene that lines of different slope can be formed. Plots of I_D/I_G against $I_{D'}/I_G$, form a straight line and depending on the slope $\sim 13, 7, 3.5$ the nature of defects in the graphene sheet can be determined to be sp^3 , vacancy or boundary defects respectively [105]. This suggests further potential for additional extractable insights from Raman spectroscopy.

1.7 Other Experimental Techniques

Brief synopses of other experimental techniques used in this work are included in Appendix C, these include: Mode of operation of laser engraver, Scanning Electron Microscopy and Fluorescence microscopy. Additionally, data analysis methods such as Design of Experiment are explained, and LabView and 3D printing programs and designs are supplied.

BIBLIOGRAPHY

- [1] L. A. Wallace, E. Pellizzari, B. Leaderer, H. Zelon, and L. Sheldon, "Emissions of volatile organic compounds from building materials and consumer products," *Atmospheric Environment* (1967), vol. 21, p. 385–393, Jan 1987.
- [2] G. Wieslander, D. Norbäck, E. Björnsson, C. Janson, and G. Boman, "Asthma and the indoor environment: the significance of emission of formaldehyde and volatile organic compounds from newly painted indoor surfaces," *International archives of occupational and environmental health*, vol. 69, p. 115–124, Dec 1997.
- [3] S. Batterman, C. Jia, and G. Hatzivasilis, "Migration of volatile organic compounds from attached garages to residences: A major exposure source," *Environmental Research*, vol. 104, p. 224–240, Jun 2007.
- [4] A. L. CLOBES, G. P. ANANTH, A. L. HOOD, J. A. SCHROEDER, and K. A. LEE, "Human activities as sources of volatile organic compounds in residential environments," *Annals of the New York Academy of Sciences*, vol. 641, p. 79–86, Apr 1992.
- [5] G. Wieslander, D. Norbäck, E. Björnsson, C. Janson, and G. Boman, "Asthma and the indoor environment: The significance of emission of formaldehyde and volatile organic compounds from newly painted indoor surfaces," *International Archives of Occupational and Environmental Health*, vol. 69, p. 115–124, Dec 1996.
- [6] Z. Z. He, K. W. Yang, C. Yu, J. Li, Q. B. Liu, W. L. Lu, Z. H. Feng, and S. J. Cai, "Improvement of Metal-Graphene Ohmic Contact Resistance in Bilayer Epitaxial Graphene Devices," *Chinese Physics Letters*, vol. 32, no. 11, 2015.
- [7] Q. Lin, Z. Gao, W. Zhu, J. Chen, and T. An, "Underestimated contribution of fugitive emission to vocs in pharmaceutical industry based on pollution characteristics, odorous activity and health risk assessment," *Journal of Environmental Sciences (China)*, vol. 126, p. 722–733, Apr 2022.
- [8] L. Zhang, J. Wang, X. Hu, J. Zhou, M. Zhao, J. Zhang, Y. Bo, Y. Huang, and Y. Zhang, "Vocs and pm concentrations in underground parking garages of the commercial center and high-rise residential buildings," *Air Quality, Atmosphere and Health*, vol. 14, p. 1117–1131, Jul 2021.
- [9] U. Schlink, M. Rehwagen, M. Damm, M. Richter, M. Borte, and O. Herbarth, "Seasonal cycle of indoor-vocs: Comparison of apartments and cities," *Atmospheric Environment*, vol. 38, no. 8, p. 1181–1190, 2004.
- [10] M. Dehghani, M. Fazlzadeh, A. Sorooshian, H. R. Tabatabaee, M. Miri, A. N. Baghani, M. Delikhoon, A. H. Mahvi, and M. Rashidi, "Characteristics and health effects of btex in a hot spot for urban pollution," *Ecotoxicology and Environmental Safety*, vol. 155, pp. 133–143, 2018.
- [11] D. of Criteria Documentation, Standards, N. I. for Occupational Safety, and H. (NIOSH), "Occupational exposure to methyl alcohol," tech. rep., 1976.
- [12] NIOSH, "Occupational health guideline for methyl alcohol," tech. rep., 1978.
- [13] N. R. Council, "Interim acute exposure guideline levels (aeglss) for methanol," Tech. Rep. 50, 2008.
- [14] J. E. Cometto-Muñiz and W. S. Cain, "Thresholds for odor and nasal pungency," *Physiology and Behavior*, vol. 48, no. 5, pp. 719–725, 1990.
- [15] J. M. Lewis, R. S. Savage, N. J. Beeching, M. B. Beadsworth, N. Feasey, and J. A. Covington, "Identifying volatile metabolite signatures for the diagnosis of bacterial respiratory tract infection using electronic nose technology: A pilot study," *PLoS ONE*, vol. 12, no. 12, p. e0188879, 2017.
- [16] F. Buljubasic and G. Buchbauer, "The scent of human diseases: A review on specific volatile organic compounds as diagnostic biomarkers," *Flavour and Fragrance Journal*, vol. 30, no. 1, pp. 5–25, 2015.
- [17] H. Kataoka, K. Saito, H. Kato, and K. Masuda, "Noninvasive analysis of volatile biomarkers in human emanations for health and early disease diagnosis," *Bioanalysis*, vol. 5, pp. 1443–1459, jun 2013.
- [18] Z. Jia, H. Zhang, C. N. Ong, A. Patra, Y. Lu, C. T. Lim, and T. Venkatesan, "Detection of Lung Cancer: Concomitant Volatile Organic Compounds and Metabolomic Profiling of Six Cancer Cell Lines of Different Histological Origins.," *ACS omega*, vol. 3, pp. 5131–5140, may 2018.

- [19] F. S. Cikach, R. A. Dweik, and R. A. Dweik, "Cardiovascular biomarkers in exhaled breath.," *Progress in cardiovascular diseases*, vol. 55, no. 1, pp. 34–43, 2012.
- [20] A. Voss, K. Witt, C. Fischer, S. Reulecke, W. Poitz, V. Kechagias, R. Surber, and H. Figulla, "Smelling heart failure from human skin odor with an electronic nose," in *2012 Annual International Conference of the IEEE Engineering in Medicine and Biology Society*, pp. 4034–4037, IEEE, aug 2012.
- [21] N. Yamane, T. Tsuda, K. Nose, A. Yamamoto, H. Ishiguro, and T. Kondo, "Relationship between skin acetone and blood β -hydroxybutyrate concentrations in diabetes," *Clinica Chimica Acta*, vol. 365, pp. 325–329, mar 2006.
- [22] K. NOSE, T. MIZUNO, N. YAMANE, T. KONDO, H. OHTANI, S. ARAKI, and T. TSUDA, "Identification of Ammonia in Gas Emanated from Human Skin and Its Correlation with That in Blood," *Analytical Sciences*, vol. 21, no. 12, pp. 1471–1474, 2005.
- [23] E. L. Dillon, M. Janghorbani, J. A. Angel, S. L. Casperson, J. J. Grady, R. J. Urban, E. Volpi, and M. Sheffield-Moore, "Novel noninvasive breath test method for screening individuals at risk for diabetes.," *Diabetes care*, vol. 32, pp. 430–5, mar 2009.
- [24] G. A. Blengini, C. E. Latunussa, U. Eynard, C. Torres de Matos, D. Wittmer, K. Georgitzikis, C. Pavel, S. Carrara, L. Mancini, M. Unguru, D. Blagoeva, F. Mathieux, and D. Pennington, *Study on the EU's list of Critical Raw Materials (2020) Final Report*. 2020.
- [25] Z. Wang, A. Ali Haidry, L. Xie, A. Zavabeti, Z. Li, W. Yin, R. Lontio Fomekong, and B. Saruhan, "Acetone sensing applications of ag modified tio2 porous nanoparticles synthesized via facile hydrothermal method," *Applied Surface Science*, vol. 533, no. July, p. 147383, 2020.
- [26] J. Bai and B. Zhou, "Titanium dioxide nanomaterials for sensor applications," *Chemical Reviews*, vol. 114, no. 19, p. 10131–10176, 2014.
- [27] C. Larrigy, M. Burke, A. Imbrogno, E. Vaughan, C. Santillo, M. Lavorgna, L. Sygellou, G. Paterakis, C. Galiotis, D. Iacopino, and A. J. Quinn, "Porous 3d graphene from sustainable materials: Laser graphitization of chitosan," *Advanced Materials Technologies*, vol. 2201228, 2022.
- [28] A. Imbrogno, J. Islam, C. Santillo, R. Castaldo, L. Sygellou, C. Larrigy, R. Murray, E. Vaughan, M. K. Hoque, A. J. Quinn, and D. Iacopino, "Laser-induced graphene supercapacitors by direct laser writing of cork natural substrates," *ACS Applied Electronic Materials*, vol. 4, no. 4, p. 1541–1551, 2022.
- [29] K. Bolotin, K. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. Stormer, "Ultrahigh electron mobility in suspended graphene," *Solid State Communications*, vol. 146, pp. 351–355, jun 2008.
- [30] G. Chen, Y. Liu, F. Liu, and X. Zhang, "Fabrication of three-dimensional graphene foam with high electrical conductivity and large adsorption capability," *Applied Surface Science*, vol. 311, pp. 808–815, aug 2014.
- [31] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, "Superior thermal conductivity of single-layer graphene," *Nano Letters*, vol. 8, no. 3, pp. 902–907, 2008.
- [32] C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene.," *Science (New York, N.Y.)*, vol. 321, pp. 385–8, jul 2008.
- [33] I. Meric, M. Y. Han, A. F. Young, B. Ozyilmaz, P. Kim, and K. L. Shepard, "Current saturation in zero-bandgap, top-gated graphene field-effect transistors," *Nature Nanotechnology*, vol. 3, pp. 654–659, nov 2008.
- [34] J. Xia, F. Chen, J. Li, and N. Tao, "Measurement of the quantum capacitance of graphene," *Nature Nanotechnology*, vol. 4, pp. 505–509, aug 2009.
- [35] X. Du, I. Skachko, A. Barker, and E. Y. Andrei, "Approaching ballistic transport in suspended graphene," *Nature Nanotechnology*, vol. 3, no. 8, pp. 491–495, 2008.
- [36] R. Murali, K. Brenner, Y. Yang, T. Beck, and J. D. Meindl, "Resistivity of graphene nanoribbon interconnects," *IEEE Electron Device Letters*, vol. 30, pp. 611–613, jun 2009.
- [37] V. B. Mohan, K.-t. Lau, D. Hui, and D. Bhattacharyya, "Graphene-based materials and their composites: A review on production, applications and product limitations," *Composites Part B: Engineering*, vol. 142, pp. 200–220, jun 2018.

- [38] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, "Detection of individual gas molecules adsorbed on graphene," *Nature Materials*, vol. 6, no. 9, pp. 652–655, 2007.
- [39] A. Kumar and C. H. Lee, "Synthesis and biomedical applications of graphene: Present and future trends," in *Advances in Graphene Science* (M. Aliofkhazraei, ed.), ch. 3, Rijeka: IntechOpen, 2013.
- [40] Y. Song, W. Zou, Q. Lu, L. Lin, Z. Liu, Y. Song, Z. Liu, W. Zou, Q. Lu, and L. Lin, "Graphene Transfer: Paving the Road for Applications of Chemical Vapor Deposition Graphene," *Small*, vol. 17, p. 2007600, dec 2021.
- [41] J. L. Melcher, K. S. Elassy, R. C. Ordonez, C. Hayashi, A. T. Ohta, and D. Garmire, "Spray-on liquid-metal electrodes for graphene field-effect transistors," *Micromachines*, vol. 10, no. 1, pp. 1–9, 2019.
- [42] L. Anzi, A. Mansouri, P. Pedrinazzi, E. Guerriero, M. Fiocco, A. Pesquera, A. Centeno, A. Zurutuza, A. Behnam, E. A. Carrion, E. Pop, and R. Sordan, "Ultra-low contact resistance in graphene devices at the Dirac point," *2D Materials*, vol. 5, no. 2, 2018.
- [43] J. N. Coleman, "Liquid-phase exfoliation of nanotubes and graphene," *Advanced Functional Materials*, vol. 19, no. 23, pp. 3680–3695, 2009.
- [44] A. Gahoi, S. Wagner, A. Bablich, S. Kataria, V. Passi, and M. C. Lemme, "Contact resistance study of various metal electrodes with cvd graphene," *Solid-State Electronics*, vol. 125, p. 234–239, Nov 2016.
- [45] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg, and R. S. Ruoff, "Transfer of cvd-grown monolayer graphene onto arbitrary substrates," *ACS Nano*, vol. 5, p. 6916–6924, Sep 2011.
- [46] K. S. Novoselov, S. V. Morozov, T. M. G. Mohinddin, L. A. Ponomarenko, D. C. Elias, R. Yang, I. I. Barbolina, P. Blake, T. J. Booth, D. Jiang, J. Giesbers, E. W. Hill, and A. K. Geim, "Electronic properties of graphene," *physica status solidi (b)*, vol. 244, p. 4106–4111, Nov 2007.
- [47] D. J. Finn, M. Lotya, G. Cunningham, R. J. Smith, D. McCloskey, J. F. Donegan, and J. N. Coleman, "Inkjet deposition of liquid-exfoliated graphene and mos2 nanosheets for printed device applications," *Journal of Materials Chemistry C*, vol. 2, no. 5, p. 925–932, 2014.
- [48] L. Niu, J. N. Coleman, H. Zhang, H. Shin, M. Chhowalla, and Z. Zheng, "Production of two-dimensional nanomaterials via liquid-based direct exfoliation," *Small*, vol. 12, no. 3, p. 272–293, 2016.
- [49] Y. Dong, S. C. Rismiller, and J. Lin, "Molecular dynamic simulation of layered graphene clusters formation from polyimides under extreme conditions," *Carbon*, vol. 104, pp. 47–55, 2016.
- [50] P. Sacchetti, "Laser formed resistor elements 4,286,250," 1981.
- [51] A. Epstein, "Electrically insulating polymer matrix with conductive path formed in situ 4,841,099," 1989.
- [52] Robert C. Binning, "Method of graphitizing fibers by laser," 1972.
- [53] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, and J. M. Tour, "Laser-induced porous graphene films from commercial polymers," *Nature Communications*, vol. 5, p. 5714, dec 2014.
- [54] R. Ye, Y. Chyan, J. Zhang, Y. Li, X. Han, C. Kittrell, and J. M. Tour, "Laser-Induced Graphene Formation on Wood," *Advanced Materials*, vol. 29, no. 37, 2017.
- [55] R. Ye, D. K. James, and J. M. Tour, "Laser-Induced Graphene: From Discovery to Translation," *Advanced Materials*, 2018.
- [56] M. Burke, C. Larrigy, E. Vaughan, G. Paterakis, L. Sygellou, A. J. Quinn, G. Herzog, C. Galiotis, and D. Iacopino, "Fabrication and electrochemical properties of three-dimensional (3d) porous graphitic and graphenelike electrodes obtained by low-cost direct laser writing methods," *ACS Omega*, vol. 5, no. 3, p. 1540–1548, 2020.
- [57] R. W. Dreyfus, "CN temperatures above laser ablated polyimide," *Applied Physics A Solids and Surfaces*, vol. 55, pp. 335–339, oct 1992.

- [58] R. Ye, D. K. James, and J. M. Tour, "Laser-Induced Graphene," *Accounts of Chemical Research*, vol. 51, no. 7, pp. 1609–1620, 2018.
- [59] J. Ma, D. Alfè, A. Michaelides, and E. Wang, "Stone-Wales defects in graphene and other planar sp^2 -bonded materials," *Physical Review B - Condensed Matter and Materials Physics*, vol. 80, no. 3, 2009.
- [60] Y. Li, D. X. Luong, J. Zhang, Y. R. Tarkunde, C. Kittrell, F. Sargunraj, Y. Ji, C. J. Arnusch, and J. M. Tour, "Laser-Induced Graphene in Controlled Atmospheres: From Superhydrophilic to Superhydrophobic Surfaces," *Advanced Materials*, vol. 29, p. 1700496, jul 2017.
- [61] N. Yamazoe, Y. Kurokawa, and T. Seiyama, "Effects of additives on semiconductor gas sensors," *Sensors and Actuators*, vol. 4, no. C, p. 283–289, 1983.
- [62] G. C. Bond, L. R. Molloy, and M. J. Fuller, "Oxidation of carbon monoxide over palladium-tin(IV) oxide catalysts: An example of spillover catalysis," *Journal of the Chemical Society, Chemical Communications*, no. 19, pp. 796–797, 1975.
- [63] D. Degler, H. W. Pereira De Carvalho, K. Kvashnina, J. D. Grunwaldt, U. Weimar, and N. Barsan, "Structure and chemistry of surface-doped Pt:SnO₂ gas sensing materials," *RSC Advances*, vol. 6, no. 34, pp. 28149–28155, 2016.
- [64] M. Hübner, D. Koziej, J. D. Grunwaldt, U. Weimar, and N. Barsan, "An au clusters related spill-over sensitization mechanism in sno₂-based gas sensors identified by operando herfd-xas, work function changes, dc resistance and catalytic conversion studies," *Physical Chemistry Chemical Physics*, vol. 14, no. 38, p. 13249–13254, 2012.
- [65] A. Gonzalez-Eliphe, J. Soria, and Q. Inorgdnica, "Electron Exchange in TiO₂-Supported Silver," *Journal of Catalysis*, vol. 76, pp. 254–264, 1982.
- [66] L. Yang, G. Zheng, Y. Cao, C. Meng, Y. Li, H. Ji, X. Chen, G. Niu, J. Yan, Y. Xue, and H. Cheng, "Moisture-resistant, stretchable NO_x gas sensors based on laser-induced graphene for environmental monitoring and breath analysis," *Microsystems and Nanoengineering*, vol. 8, no. 1, 2022.
- [67] R. Bogue, "Nanomaterials for gas sensing: A review of recent research," *Sensor Review*, vol. 34, no. 1, pp. 1–8, 2014.
- [68] T. Hussain, M. Sajjad, D. Singh, H. Bae, H. Lee, J. A. Larsson, R. Ahuja, and A. Karton, "Sensing of volatile organic compounds on two-dimensional nitrogenated holey graphene , graphdiyne , and their heterostructure," *Carbon*, vol. 163, pp. 213–223, 2020.
- [69] S. H. K. Yap, K. K. Chan, S. C. Tjin, and K. T. Yong, "Carbon allotrope-based optical fibers for environmental and biological sensing: A review," *Sensors (Switzerland)*, vol. 20, no. 7, 2020.
- [70] D. Pawar, R. Kanawade, A. Kumar, C. N. Rao, P. Cao, S. Gaware, D. Late, S. N. Kale, S. T. Navale, W. J. Liu, D. L. Zhu, Y. M. Lu, and R. K. Sinha, "High-performance dual cavity-interferometric volatile gas sensor utilizing Graphene/PMMA nanocomposite," *Sensors and Actuators, B: Chemical*, vol. 312, no. November 2019, 2020.
- [71] W. Chen, Z. Wang, S. Gu, J. Wang, Y. Wang, and Z. Wei, "Hydrophobic amino-functionalized graphene oxide nanocomposite for aldehydes detection in fish fillets," *Sensors and Actuators, B: Chemical*, vol. 306, no. December 2019, p. 127579, 2020.
- [72] A. Leong, T. Saha, V. Swamy, and N. Ramakrishnan, "A langasite crystal microbalance coated with graphene oxide-platinum nanocomposite as a volatile organic compound sensor: Detection and discrimination characteristics," *Sensors (Switzerland)*, vol. 20, no. 2, 2020.
- [73] J. S. Jang, J. Lee, W. T. Koo, D. H. Kim, H. J. Cho, H. Shin, and I. D. Kim, "Pore-Size-Tuned Graphene Oxide Membrane as a Selective Molecular Sieving Layer: Toward Ultrasensitive Chemiresistors," *Analytical Chemistry*, vol. 92, no. 1, pp. 957–965, 2020.
- [74] A. Yavarinasab, S. Janfaza, N. Tasnim, H. Tahmooressi, A. Dalili, and M. Hoorfar, "Graphene/poly (methyl methacrylate) electrochemical impedance-transduced chemiresistor for detection of volatile organic compounds in aqueous medium," *Analytica Chimica Acta*, vol. 1109, pp. 27–36, 2020.

- [75] J. W. Yoon and J. H. Lee, "Toward breath analysis on a chip for disease diagnosis using semiconductor-based chemiresistors: Recent progress and future perspectives," *Lab on a Chip*, vol. 17, no. 21, pp. 3537–3557, 2017.
- [76] H. Choi, H. Y. Jeong, D.-S. Lee, C.-G. Choi, and S.-Y. Choi, "Flexible NO₂ gas sensor using multilayer graphene films by chemical vapor deposition," *Carbon letters*, vol. 14, no. 3, pp. 186–189, 2013.
- [77] E. C. Mattson, K. Pande, M. Unger, S. Cui, G. Lu, M. Gajdardziska-Josifovska, M. Weinert, J. Chen, and C. J. Hirschmugl, "Exploring adsorption and reactivity of NH₃ on reduced graphene oxide," *Journal of Physical Chemistry C*, vol. 117, no. 20, pp. 10698–10707, 2013.
- [78] M. Shekhirev, A. Lipatov, A. Torres, N. S. Vorobeve, A. Harkleroad, A. Lashkov, V. Sysoev, and A. Sinitskii, "Highly Selective Gas Sensors Based on Graphene Nanoribbons Grown by Chemical Vapor Deposition," *ACS Applied Materials and Interfaces*, vol. 12, no. 6, pp. 7392–7402, 2020.
- [79] J. Wu, K. Tao, Y. Y. Guo, Z. Li, X. T. Wang, Z. Z. Luo, S. L. Feng, C. L. Du, D. Chen, J. M. Miao, and L. K. Norford, "A 3D chemically modified graphene hydrogel for fast, highly sensitive, and selective gas sensor," *Advanced Science*, vol. 4, no. 3, pp. 1–10, 2017.
- [80] A. K. Basu, A. N. Sah, M. M. Dubey, P. K. Dwivedi, A. Pradhan, and S. Bhattacharya, "MWCNT and α -Fe₂O₃ embedded rGO-nanosheets based hybrid structure for room temperature chloroform detection using fast response/recovery cantilever based sensors," *Sensors and Actuators, B: Chemical*, vol. 305, no. November 2019, p. 127457, 2020.
- [81] F. Yavari, Z. Chen, A. V. Thomas, W. Ren, H. M. Cheng, and N. Koratkar, "High sensitivity gas detection using a macroscopic three-dimensional graphene foam network," *Scientific Reports*, vol. 1, pp. 1–5, 2011.
- [82] T. T. Tung, M. T. Tran, J. F. Feller, M. Castro, T. Van Ngo, K. Hassan, M. J. Nine, and D. Losic, "Graphene and metal organic frameworks (MOFs) hybridization for tunable chemoresistive sensors for detection of volatile organic compounds (VOCs) biomarkers," *Carbon*, vol. 159, pp. 333–344, 2020.
- [83] T. Seiyama, K. Fujiishi, M. Nagatani, and A. Kato, "A New Detector for Gaseous Components Using Zinc Oxide Thin Films," *The Journal of the Society of Chemical Industry, Japan*, vol. 66, no. 5, pp. 652–655, 1963.
- [84] P. J. Shaver, "Activated tungsten oxide gas detectors," *Applied Physics Letters*, vol. 11, no. 8, pp. 255–257, 1967.
- [85] J. L. Johnson, A. Behnam, S. J. Pearton, and A. Ural, "Hydrogen sensing using Pd-functionalized multi-layer graphene nanoribbon networks," *Advanced Materials*, vol. 22, no. 43, pp. 4877–4880, 2010.
- [86] R. Ghanbari, R. Safaiee, M. H. Sheikhi, and M. M. Golshan, "Graphene Decorated with Silver Nanoparticles as a Low-Temperature Methane Gas Sensor," *ACS Applied Materials and Interfaces*, vol. 11, pp. 21795–21806, 2019.
- [87] Q. Huang, D. Zeng, H. Li, and C. Xie, "Room temperature formaldehyde sensors with enhanced performance, fast response and recovery based on zinc oxide quantum dots/graphene nanocomposites," *Nanoscale*, vol. 4, no. 18, pp. 5651–5658, 2012.
- [88] T. Seiyama, A. Kato, K. Fujiishi, and M. Nagatani, "A new detector for gaseous components using semiconductive thin films," *Analytical Chemistry*, vol. 34, no. 11, p. 1502–1503, 1962.
- [89] N. Yamazoe, J. Fuchigami, M. Kishikawa, and T. Seiyama, "Interactions of tin oxide surface with O₂, H₂O AND H₂," *Surface Science*, vol. 86, no. C, pp. 335–344, 1979.
- [90] P. T. Moseley and D. E. Williams, "A selective ammonia sensor," *Sensors and Actuators: B. Chemical*, vol. 1, no. 1-6, pp. 113–115, 1990.
- [91] S. J. Kim, I. S. Hwang, C. W. Na, I. D. Kim, Y. C. Kang, and J. H. Lee, "Ultrasensitive and selective c₂h₅oh sensors using rh-loaded in₂o₃ hollow spheres," *Journal of Materials Chemistry*, vol. 21, no. 46, p. 18560–18567, 2011.
- [92] J. W. Yoon, J. K. Choi, and J. H. Lee, "Design of a highly sensitive and selective c₂h₅oh sensor using p-type co₃o₄ nanofibers," *Sensors and Actuators, B: Chemical*, vol. 161, no. 1, p. 570–577, 2012.

- [93] M. Hübner, C. E. Simion, A. Tomescu-Stănoiu, S. Pokhrel, N. Bârsan, and U. Weimar, "Influence of humidity on co sensing with p-type cuo thick film gas sensors," *Sensors and Actuators, B: Chemical*, vol. 153, no. 2, p. 347–353, 2011.
- [94] S. Pokhrel, C. E. Simion, V. Quemener, N. Bârsan, and U. Weimar, "Investigations of conduction mechanism in cr2o3 gas sensing thick films by ac impedance spectroscopy and work function changes measurements," *Sensors and Actuators, B: Chemical*, vol. 133, no. 1, p. 78–83, 2008.
- [95] C. Wang, J. Liu, Q. Yang, P. Sun, Y. Gao, F. Liu, J. Zheng, and G. Lu, "Ultrasensitive and low detection limit of acetone gas sensor based on w-doped nio hierarchical nanostructure," *Sensors and Actuators, B: Chemical*, vol. 220, p. 59–67, 2015.
- [96] T. Seiyama and S. Kagawa, "Study on a detector for gaseous components using semiconductive thin films," *Analytical Chemistry*, vol. 38, no. 8, p. 1069–1073, 1966.
- [97] N. Yamazoe, "New approaches for improving semiconductor gas sensors," *Sensors and Actuators: B. Chemical*, vol. 5, no. 1–4, p. 7–19, 1991.
- [98] N. Barsan, C. Simion, T. Heine, S. Pokhrel, and U. Weimar, "Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors," *Journal of Electroceramics*, vol. 25, no. 1, p. 11–19, 2010.
- [99] N. Barsan and U. Weimar, "Conduction model of metal oxide gas sensors," *Journal of Electroceramics*, vol. 7, no. 3, p. 143–167, 2001.
- [100] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films.," *Science (New York, N.Y.)*, vol. 306, pp. 666–9, oct 2004.
- [101] K. N. Parrish and D. Akinwande, "Impact of contact resistance on the transconductance and linearity of graphene transistors," *Applied Physics Letters*, vol. 98, no. 18, 2011.
- [102] A. C. Ferrari and D. M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of graphene," *Nature Nanotechnology*, vol. 8, no. 4, p. 235–246, 2013.
- [103] L. M. Malard, M. A. Pimenta, G. Dresselhaus, and M. S. Dresselhaus, "Raman spectroscopy in graphene," *Physics Reports*, vol. 473, pp. 51–87, apr 2009.
- [104] P. Venezuela, M. Lazzeri, and F. Mauri, "Theory of double-resonant Raman spectra in graphene: Intensity and line shape of defect-induced and two-phonon bands," *Physical Review B*, vol. 84, p. 035433, jul 2011.
- [105] A. Eckmann, A. Felten, A. Mishchenko, L. Britnell, R. Krupke, K. S. Novoselov, and C. Casiraghi, "Probing the nature of defects in graphene by Raman spectroscopy," *Nano Letters*, vol. 12, no. 8, pp. 3925–3930, 2012.
- [106] D. M. Basko, "Theory of resonant multiphonon Raman scattering in graphene," *Physical Review B*, vol. 78, p. 125418, sep 2008.
- [107] D. Yoon, H. Moon, H. Cheong, J. Sik Choi, J. Ae Choi, and B. Ho Park, "Variations in the Raman Spectrum as a Function of the Number of Graphene Layers," *Journal of the Korean Physical Society*, vol. 55, no. 3, 2009.
- [108] J.-B. Wu, M.-L. Lin, X. Cong, H.-N. Liu, and P.-H. Tan, "Raman spectroscopy of graphene-based materials and its applications in related devices," *Chemical Society Reviews*, vol. 47, pp. 1822–1873, mar 2018.
- [109] Z. Sun, A.-R. O. Raji, Y. Zhu, C. Xiang, Z. Yan, C. Kittrell, E. L. G. Samuel, and J. M. Tour, "Large-Area Bernal-Stacked Bi-, Tri-, and Tetralayer Graphene," *ACS Nano*, vol. 6, pp. 9790–9796, nov 2012.
- [110] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, "Raman Spectrum of Graphene and Graphene Layers," *Physical Review Letters*, vol. 97, p. 187401, oct 2006.
- [111] Y. Hao, Y. Wang, L. Wang, Z. Ni, Z. Wang, R. Wang, C. K. Koo, Z. Shen, and J. T. L. Thong, "Probing Layer Number and Stacking Order of Few-Layer Graphene by Raman Spectroscopy," *Small*, vol. 6, pp. 195–200, jan 2010.

- [112] A. M. Dimiev, G. Ceriotti, N. Behabtu, D. Zakhidov, M. Pasquali, R. Saito, and J. M. Tour, "Direct Real-Time Monitoring of Stage Transitions in Graphite Intercalation Compounds," *ACS Nano*, vol. 7, pp. 2773–2780, mar 2013.

DESIGN OF EXPERIMENTS AND OPTIMIZATION OF LASER-INDUCED GRAPHENE-LIKE CARBON

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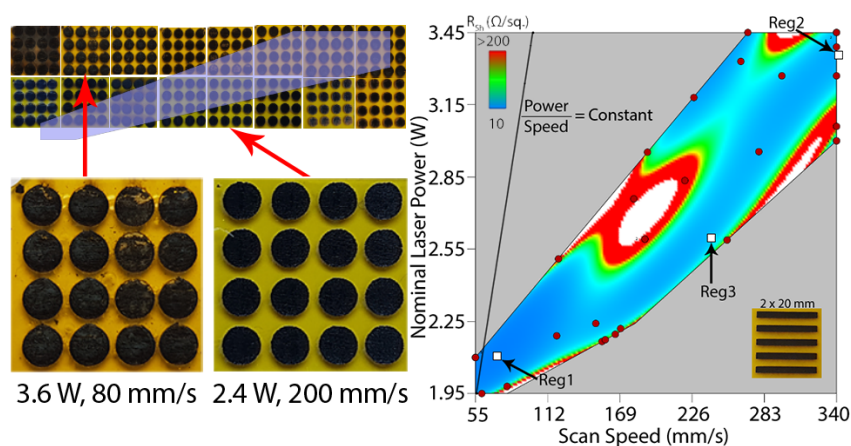


Table of Contents Figure for Design of Experiments and Optimization of Laser-Induced Graphene

2.1 Contributions to Knowledge

This paper focuses on the development of robust and generalisable optimisation routines for LIG material. Contemporaneous investigations of LIG used high cost equipment and one-factor at a time investigations methods and often yield high resistance, defective LIG material. Typical optimisation routes at this time followed one-factor at a time optimisation routes, limiting the number of factors included and increasing experimental cost.

This work demonstrated the formation of LIG using a low cost hobbyist laser system $\sim \$500$, and its subsequent optimisation through an iterative design of experiment process to achieve the lowest sheet resistance reported at the time of publication $\sim 15 \text{ Ohm/sq.}$. A visual grading method was developed to screen potentially viable laser conditions. Similarly, a resource efficient sheet resistance estimation route was demonstrated to facilitate high experimental throughput.

Together these rapid screening techniques facilitated the implementation of a system-agnostic multifactor, iterative design of experiment optimisation route for LIG. The general applicability of the optimisation route is demonstrated by implementation on a novel, and more complex, laser system. The benefit of the method was demonstrated by the discovery of high throughput-low sheet resistance formation conditions at non-intuitive laser parameters. Further, this work contains the first reported demonstration of *Eckmann et al.* Raman analysis method for determining defect types in graphene-type material examined on the potential optima parameters determined [41]. Finally, I report the first demonstration of an all-polymer and LIG-based humidity sensors.

Abstract

Realization of graphene-based sensors and electronic devices remains challenging; in part due to integration challenges with current fabrication and manufacturing processes. Thus, scalable methods for *in situ* fabrication of high-quality graphene-like materials are essential. Low-cost CO₂ laser engravers can be used for site-selective conversion of polyimide under ambient conditions to create 3D, rotationally disordered few-layer, porous, graphene-like electrodes. However, the exact parameter dependencies of laser power and scan speed on the graphitization process are not well understood, presenting challenges for rapid, resource-efficient optimization.

An iterative optimization strategy was developed to identify promising regions in the power-speed parameter space, with the goal of optimizing electrode performance while maximizing scan speed and hence fabrication throughput. The strategy employed iterations of DoE-RS methods combined with choices of readily measurable parameters to minimize measurement resources and time. The Initial DoE-RS experiment set employed visual response parameters while subsequent iterations used sheet resistance as the optimization parameter. The final model clearly demonstrates that laser graphitization is a highly non-linear process requiring polynomial terms in scan speed and laser power up to fifth order.

Two regions of interest were identified using this strategy. A global minimum (~ 16 ohm/sq.) was found for sheet resistance at low scan speed (70 mm/s, 2.1 W, Region 1) and a local minimum sheet resistance at higher scan speed of 36 ohms/sq. (340 mm/s, 3.4 W, Region 2), allowing ~ 5 -fold reduction in write time. Importantly, these minima do not correspond to constant ratios of laser power to scan speed. This highlights the benefits of DoE-RS methods in rapid identification of optimum parameter combinations that would be difficult to discover using traditional one-factor-at-a-time optimization.

Verification data from Raman spectroscopy showed sharp 2D peaks with mean full-width-at-half-maximum intensity values $< 80 \text{ cm}^{-1}$ for both regions, indicative of high-quality graphene-like carbon. Graphene-based electrodes fabricated using the parameters from the respective regions yielded similar performance when employed as capacitive humidity sensors with hygroscopic dielectric layers. Devices fabricated using Region 1 parameters (16 Ohm/sq.) yielded capacitance responses of $0.78 \pm 0.04 \text{ pF}$ at 0% Relative Humidity

(RH), increasing to $31 \pm 7 \text{ pF}$ at 85.1% RH. Region 2 devices showed comparable responses ($0.88 \pm 0.04 \text{ pF}$ at 0% RH, $28 \pm 5 \text{ pF}$ at 85.1% RH).

2.2 Introduction and Theory

Graphene and graphene-like materials, since their discovery, have been an exciting area of investigation for material science. High carrier mobility, thermal conductivity, tensile strength, zero bandgap and ballistic transport have been demonstrated, for the most part in micron-scale pristine monolayer graphene, usually created by mechanical exfoliation. [1–7] This slow, non-scalable method hinders application development, such as graphene-based sensors. [8–10]

Several routes have been proposed to develop graphene-like materials with methods suited to scalable fabrication. Examples include CVD graphene, reduced graphene oxide, and liquid phase exfoliated graphene. Each approach can be assessed in terms of graphene quality and throughput. Transfer of CVD-grown mono- or few-layer graphene from metal catalyst foil substrates (~ 1 -100 cm lateral dimensions) typically requires long processing times and the use of protective polymer handling layers. Residue from these layers presents challenges including unintentional heterogeneous doping and also tunnel barriers which can cause large contact resistance. Typical sheet resistance values usually exceed $500 \Omega/sq.$ for air-stable devices, consistent with the expected reduction in sheet resistance from pristine monolayer graphene ($\sim 6 k\Omega/sq.$ measured in vacuum for mechanically exfoliated monolayers) due to adsorbate doping from ambient water vapor or process residue. [11–13]

Liquid-based dispersions of graphene-derived nanomaterials such as reduced graphene oxide or liquid-phase exfoliated graphene offer ease of processing and compatibility with printing methods. However, the small crystallite size (35 – 600 nm) and the presence of process-induced basal plane and edge defects result in increased sheet resistance ($2 k\Omega/sq.$) and variability. [14] Further, post-deposition curing (250 – 500 °C) is usually required which can also present challenges for some applications. [15]

Laser graphitization of polymers (often termed LIG) is a promising alternative for direct-write fabrication of porous 3D graphene-like electrodes. Although the production of graphitic material through laser graphitization has been awarded patents as far back as 1972, they achieved little insight into the resulting material. [16, 17] The most popular process is laser graphitization of polyimide using CO₂ lasers, reported by *Tour et al.* in 2014. [18] The local high-temperature and high-pressure environment created by the laser photons breaks C–O, C=O and C–N bonds

of the polyimide, producing high-pressure gas pockets that drive formation of micropores, nanopores and other structural defects, resulting in a porous 3D structure that could not be achieved through annealing alone. [19–21]

Raman spectroscopy revealed well-resolved, narrow D, G and 2D lineshapes, consistent with formation of graphitic carbon with low disorder. Significant I_{2D}/I_G ratios and a distinct shoulder in the G lineshape (corresponding to a D' defect peak) are characteristic of high-quality graphene-like carbon. The symmetric 2D lineshape contrasts with the asymmetric 2D peak reported for Bernal-stacked (ABAB) multilayer graphene or graphite, [22,23] and suggests that laser-fabricated graphene is more likely to comprise few-layer graphene structures with rotational and/or vertical stacking disorder. This distinguishes LIG from pristine mono-layer graphene, which comprises of individual, defect free, hexagonal lattices of carbon atoms.

Laser graphitization thus represents an exciting technology for direct integration of graphene-like carbon electrodes on polymer substrates. While the most promising feedstock material is polyimide, Tour and co-workers as well as other groups have demonstrated formation of graphene-like carbon using a range of synthetic polymers and natural materials, including wood, food, textiles, charcoal and anthracite coal. [24–26] To achieve these conversions, multiple-laser passes at reduced fluences, including use of defocused lasers to enhance laser-path overlap, are used to produce suitable quality LIG. [27] For each feedstock material, optimization of the laser graphitization process involves identification of a suitable set (or range) of process parameters, including laser power and scan speed that will yield direct-write formation of 3D porous, graphene-like carbon. Non-optimal laser parameters can lead to unwanted side effects from over- or under-exposure. Over-exposure effects include material ablation, re-deposition, oxidation (ashing) or combinations of these. Under-exposure effects include melting and/or incomplete graphitization. This complex materials challenge mandates optimization strategies that are both rigorous and efficient.

This optimization challenge can be addressed using Machine Learning (ML) methods [28–31], which require large datasets, or statistically driven methods, such as DoE [32]. ML methods have gained increased popularity as computational resources have increased, removing their previous analysis bottleneck. They come in many different varieties each depending on different

algorithms for modelling supplied data. Datasets containing numerous potential factors that require both reduced dimensionality and modelling may benefit from Principal Component Regression, while highly intricate systems may be more easily modelled by an ensemble method like Random Forests. More generic approaches could be used to facilitate more rapid model preparation, such as Neural Networks. For resource-constrained applications, the major drawback for ML is the requirement for large datasets of training data to produce a model. [28–31]

Resource-efficient optimization mandates minimization of resources (including time) used to generate and analyze data. ML methods reduce the analysis load, but increase the required dataset size, and hence the resources required to produce those samples. DoE methods extract maximum information from a lean, statistically significant dataset. DoE ensures that minimal samples are produced – reducing experimental cost – while ensuring that sufficient samples are tested to account for variability. The decreased number of samples required to be produced and tested comes at the cost of increased analysis.

The distinction between ML and DoE methods is clear; when large datasets are readily available then ML should be preferred, if samples are resource intensive then DoE methods are preferable. Highly complex systems can be simplified through iterative implementation of DoE methods. Each simplification step screens out insignificant factors and target parameter ranges of interest. This stepwise process allows for dynamic decision making and scaled resource commitment not possible through less agile investigative tools. Similarly, DoE produces a documented search path with explicitly defined assumptions, not always generated with ML. Therefore, initial screening experiments followed by informed, iterative optimization requires less resources than an equivalent ML study.

Here we report on an iterative DoE-RS strategy for identification of promising regions in the laser power vs. scan speed parameter space, with the goal of optimizing electrode performance while maximizing scan speed and hence fabrication throughput. DoE-RS optimization methods are well recognized as significantly more efficient than traditional one-factor-at-a-time methods. Further, DoE-RS approaches enable rigorous optimization even when there are non-linear interdependencies between input parameters. [33–35] DoE-RS approaches enable additional statistical efficiency by utilizing non-rectangular regions in parameter space to avoid non-viable

regions with the added benefit of reduced experimental cost (resources and time).

Each iteration of the strategy focused on a readily measurable parameter to further minimize measurement resources and time. The initial DoE-RS iteration employed visual response parameters while subsequent DoE-RS iterations optimized sheet resistance. We note that optimization strategies for graphene-based electronic or electrochemical sensing elements often include minimizing access resistance as a target, in order to reduce iR potential drops that can diminish sensor performance, and also energy efficiency. [36] Finally, we report on an iterative DoE screening approach to identify key laser parameters and parameter interactions for a more sophisticated laser system, where the user has additional control over beam overlap within the raster pattern.

Since LIG electrodes and structures are produced by a dynamic patterning process which involves both temporal modulation of the laser output (through the duty cycle) and spatial patterning (through displacement of the laser head), optimization requires consideration of potential non-linear contributions of user-controlled parameters, including average laser power and scan speed, as well as potential interaction effects between these parameters.

2.3 Methodology

2.3.1 Sample Preparation and Visual Inspection

A low cost ($\sim$ \$500) CO₂ laser engraver [10.6 μ m wavelength, 0-30 W power, (oscillating mirror modulation), HQ-3020B, GuangZhou Amonstar Trade Co. Ltd] was rastered under ambient conditions to convert adhesive backed polyimide film (Radionics, HB830-19, thickness: 70 μ m), supported by an acrylic substrate, into graphitic material. A parameter space of 6 laser power values in the range 2.4-8.4 W and 11 scan speed values in the range 40-440 mm/s was investigated by producing a series of samples on polyimide for a subset of 60 combinations of laser power and scan speed as shown in Figure SI-2.1. Each sample (16 discs, each 4 mm diameter) was visually inspected to determine the bounds of the uniform, black, non-damaged material - a useful visual indicator for LIG.

2.3.2 Iterative Design of Experiments Methods

The region of interest derived from the visual inspection was used to define a screening DoE response surface (DoE-RS, Design Expert 11) based on visually graded responses (fibrosity, redeposited residue, damage) as assessed on a scale 1-10 (Figure SI-2.2). Informed by this visual screening DoE-RS, a further 18-point screening DoE-RS using a sheet resistance response factor was constructed, as shown in Figure SI-2.3. Transfer line measurement tracks of length 1.5-6 mm at widths of 0.5-1.8 mm were produced. The resistances were recorded using a multimeter (Fluke 179) and the corresponding sheet resistances extracted. The average sheet resistance from five transfer line measurement structures was used for the DoE-RS. Predicted optima at low-moderate laser power and scan speed was investigated by a subsequent 30-point DoE-RS, using a sheet resistance response. Each sample for this final DoE-RS comprised five replicates of 20 mm $\times$ 2 mm bar structures (10:1 aspect ratio). The use of long, high aspect ratio bar structures minimizes the influence of contact resistance, by ensuring it is a small proportion of the total recorded resistance, while retaining high throughput of measurements. The inclusion of replicates was to account for any variability in the contact resistance. A DoE-RS model was constructed using an inverse transformation and fifth-order polynomial terms, as described in Section SI-2.2.

Three regions of interest were identified from the final response surface experiments (Region 1, Region 2, Region 3). Five replicates of the 20 mm $\times$ 2 mm structures were produced using the DoE-RS model parameters for that region. Current-voltage sweeps (-3 V to +3 V) were acquired (Desert cryogenic probe station with Agilent E4980A parameter analyzer) to verify the multimeter measurements. The associated sheet resistance values were calculated.

2.3.3 Raman Spectroscopy Measurements and Analysis

Samples produced under the Region 1, Region 2 and Region 3 conditions, were characterized by Raman spectroscopy mapping (Reinshaw inVia, 514.5nm Ar laser, 20 $\times$, 50 $\times$ objectives). To account for the 3D structure and sample inhomogeneity numerous scans were taken as part of a Raman map of each region. Mapping was conducted at 20 $\times$ and 50 $\times$ magnifications at three spatially distinct areas across two separate samples. 228 scans were conducted for Region

1 samples, 230 for Region 2 samples and 219 for region 3 samples. All scans for Region 1 and Region 2 samples displayed graphitic behavior. For Region 3 samples, 70% of the spectra showed graphitic peaks (158 of 219); the remaining 61 displayed only the background associated with scattering from a highly 3D sample.

Of the scans that displayed graphitic behavior, 14 spectra were randomly selected for detailed peak fitting. Spectra from Region 1 and Region 2 samples were fit with six Lorentzian peaks – three first order Raman peaks (D, G, D') and three second order (D + D'', 2D, D+ D'). Spectra from Region 3 samples were fit with 4 peaks, since the D' and D + D'' peaks could not be resolved. The mm-scale and microscale morphology of the samples was characterized by Scanning Electron Microscopy (SEM, JSM-6700F JEOL UK Ltd.).

2.3.4 Humidity Sensing

Interdigitated electrodes were fabricated using the predicted DoE-RS parameters for two minima: the global minimum sheet resistance (Region 1) and minimum sheet resistance at high scan speed (Region 2). Polyvinyl alcohol (PVA) was doctor-bladed onto the electrodes to create a hygroscopic dielectric layer for proof-of-concept capacitance-based humidity sensors. The capacitance sensors (six individual devices for each region) were equilibrated for 6 h above saturated salt solutions, producing standard humidity environments according to the E104-02 standard, i.e. Vacuum: 0% relative humidity (RH); MgCl: 33.1% RH; K₂CO₃: 43.2% RH; NaCl: 75.5% RH; KCl 85.1% RH. [37] The capacitance response was measured using an AC potential sweep (Agilent E53708B LCR Meter, 2 kHz).

2.4 Results and Discussion

In the first report of LIG, Tour et al. observed a dependence of sheet resistance on laser power with a threshold of 2.4 W at ~ 90 mm/s using a Universal Laser System X-660 laser cutter platform and achieved minimum sheet resistances at 5.4 W, 90 mm/s through OFAT optimization. These authors also noted that a linear dependence of the threshold power for graphitization on the scan speed. [18] This observed interaction of factors suggests that both laser power and scan speed should be considered simultaneously, as underlying mechanisms may not be observable through OFAT methods.

DoE methods are implemented in this work to illustrate their ability to determine relationships between factors in a material synthesis, and be used to rapidly, and incrementally optimize the material. Initially, samples were visually inspected to identify laser power and scan speed parameters which yielded unviable samples, e.g. cracked inhomogeneous graphitic material (Figure 2.1a) and parameters which yielded homogeneous, deep black material (Figure 2.1b). The visual inspection was further refined through a DoE-RS process, based on qualitatively measured visual responses (fibrosity, residue and damage), as seen in Figure SI-2.2. The model indicated that lower laser power (2.4-3.9 W for our hobbyist laser system) and higher scan speed (280-440 mm/s) yielded fewer defects. A subsequent sheet resistance-based DoE-RS (Figure SI-2.3) showed a region of low sheet resistance at low laser power (2.4-5.4 W) and moderate scan speed (200-440 mm/s) that tapers as laser power and scan speed increase. This model suggested that the global sheet resistance minimum for this laser system could be found at even lower scan speed and laser power, which informed the parameter ranges used in the final iteration DoE-RS (Figure 2.1d).

The response surface model is based on a polynomial fit built from statistically significant terms (Table SI-2.4). Up to fifth order terms in scan speed and fourth order terms of laser power were seen to be significant. Lower-order terms and cross terms were also included. Table SI-2.5 shows the significance of each term. The p-value (<0.0001) for the final model confirms the statistical significance of the terms. Further, the residual lack of fit was insignificant (p-value of 0.44), suggesting confidence in the model chosen and its predictions. Response surface zones colored in white could not be fit with the model, likely indicating non-viable conditions for

graphitization or low-quality material. Three specific “regions of interest” are labelled on the response surface: The predicted global minimum sheet resistance (Region 1), a local minimum at high scan speed (Region 2) and an interim point (Region 3).

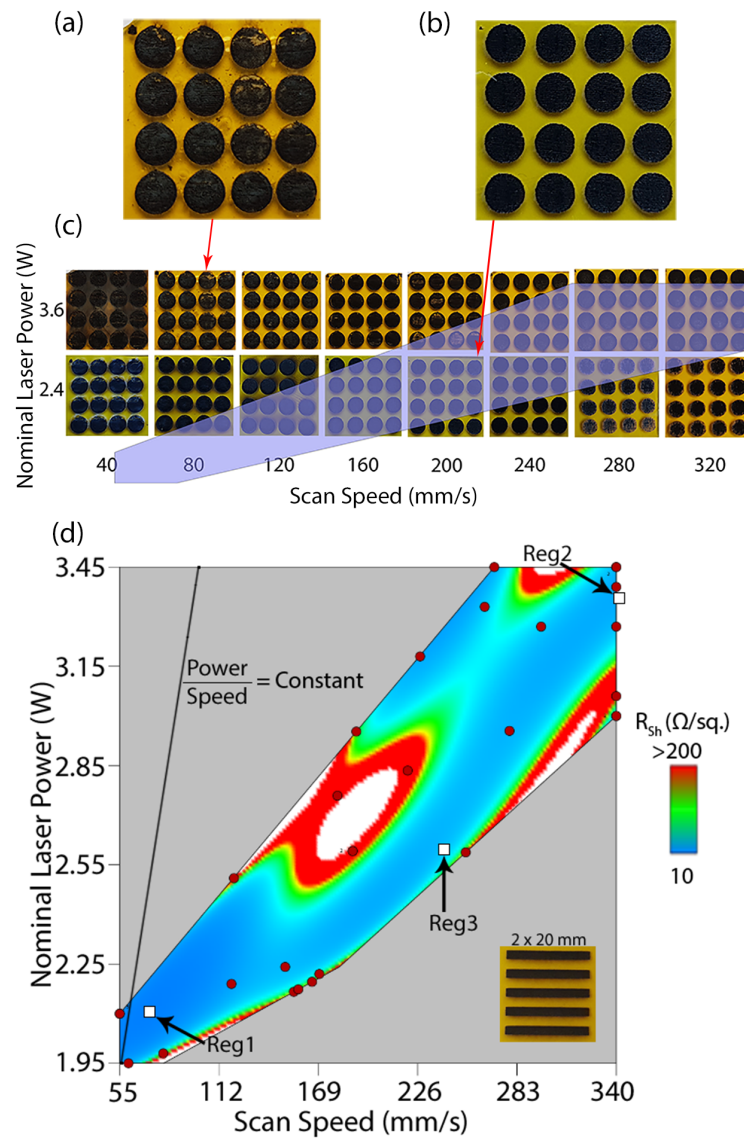


Figure 2.1: a) Photo of visual inspection test structures (4 mm diameter discs) which show laser-induced defects such as cracks and delamination. Laser parameters: 80 mm/s raster scan speed, 3.6 W power b). Set of discs showing uniform, black material (200 mm/s scan speed, 2.4 W). c). Subset of the overall grid layout of test structure photos organized by scan speed and laser power (full layout in Figure SI-2.1). The shaded region shows the final Response Surface parameter domain. d) DoE-RS model output for sheet resistance vs laser power and raster scan speed factors. Arrows indicate the Regions of Interest for further characterization: global minimum for sheet resistance (Reg. 1); minimum sheet resistance at high scan speed (Reg. 2) and a local minimum resistance at intermediate scan speed (Reg. 3). Inset: Photo of array of 20 mm x 2 mm test structures used for sheet resistance measurements.

Table 2.1: Predicted and actual sheet resistance values from linear I-V plots from -3 V to 3 V of region of interest test points.

Region	Laser Power (W)	Scan Speed (mm/s)	Predicted Sheet Res. ($\Omega/sq.$)	Mean Sheet Res. ($\Omega/sq.$)
1	2.1	70	10	15.7 ± 0.7
2	3.4	340	26	36 ± 1
3	2.6	240	37	410 ± 180

Table 2.1 shows the predicted sheet resistances for three regions of interest and the corresponding experimental sheet resistance values. Region 1 and Region 2 samples yield predicted and measured sheet resistance values that agree within a factor 2. Importantly, the model allows identification of Region 2, where low sheet resistance can still be achieved while increasing scan speed by a factor 5. The measured sheet resistance for Region 3 is over an order of magnitude higher than the predicted model value. This discrepancy could be due to the high curvature of the model in this zone of the parameter space, where a small fluctuation of the laser parameters could result in a large change in sheet resistance.

Figure 2.2 shows the morphology associated with the three regions of interest. A hierarchical pore structure with micron-scale and sub-micron pore diameters can be observed in samples fabricated using parameters for Region 1 (Fig. 2.2a,b) and for Region 2 (Fig.2.2c,d). In addition, the Region 2 sample also shows a higher density of 3D extrusions. The morphology of the Region 3 sample differs markedly from the samples for Regions 1 and 2. There is no longer a clear porosity, instead the surface comprises sub-mm 3D extrusions (Fig. 2.2e) comprising networks of micron-scale fibers (Figure 2.2f).

Cross-sectional SEM Micrographs show approximate LIG thickness of $50 \mu m$ (Figure SI-2.6). This agrees with thickness values observed by Duy et al., who noted LIG thickness self-limits to $<50 \mu m$. The maximum conversion depth is caused by the conversion beginning at the surface, attenuating the conversion of the sub-surface material. [27] As such, it is assumed that both Region 1 and Region 2 materials are of approximately the same thickness. However, as is seen in Figure 2.2c the region 2 material contains vertical extrusions. These structures could reduce the available lateral charge-transfer pathways and are likely partly responsible for the reduced conductivity of Region 2 materials. Assuming an LIG thickness of $50 \mu m$, the corresponding resistivity for Region 1 material is $7.8 \times 10^{-4} \Omega m$, reflecting the expected disorder on the device

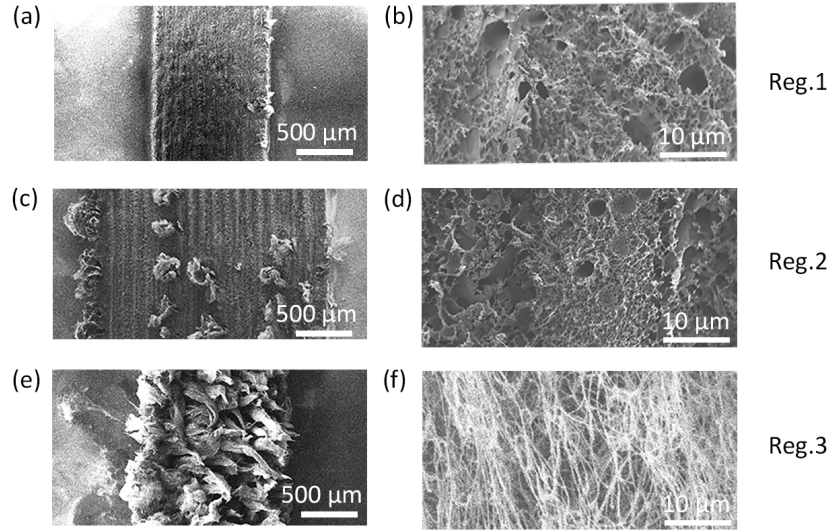


Figure 2.2: SEM data at low and higher magnifications, respectively, for samples fabricated using parameters from region 1 (a,b); region 2 (c,d) and region 3 (e, f).

length scale (2cm).

Stamatin et al. have reported on the morphology of laser-graphitized polyimide in terms of a similar metric: [38]

$$\text{Dynamic Fluence} = \frac{\text{Laser Power}}{\text{Scan Speed} \times \text{Beam Diameter}} \quad (2.1)$$

They calculated dynamic fluence values from 0.3 to 4.8 J/mm². For this work, initial rough estimates of dynamic fluence can be made using the raster pitch as the beam diameter ($\sim 90\mu\text{m}$ for the region 1 material, see Figure 2.2a). In this way, the initial estimates of dynamic fluence are 0.33 J/mm² (region 1), 0.11 J/mm² (region 2), 0.12 J/mm² (region 3).

However, dynamic fluence values consider only single laser passes without accounting for overlap of subsequent raster lines. The line-line overlap is estimated in the as $\sim 85\mu\text{m}$ from Figure SI-2.8. Tour et al., as previously noted, demonstrated that multi-pass lasing can produce LIG even at reduced laser intensities upon subsequent re-exposure. [27] Consequently, a reduction of dynamic fluence values, relative to those seen by Stamatin et al. is expected due to the beam overlap from rastering.

Moreover, the fact that Regions 1 and 2 do not lie on a line of constant Laser Power/Scan Speed (solid line in Figure 2.1d) highlights the non-linearity of the parameter dependencies for laser graphitization, which would not be uncovered by traditional OFAT optimization. This is especially significant as the beam profile can vary with laser power, further convolving any laser

power dependence and any overlap dependence. This increases the complexity of investigating the parameter space and highlights the potential of DoE-RS methods to facilitate optimisation, especially for resource-constrained processes. It allowed us to achieve similar sheet resistance value but with a five-fold increase in scan speed, and hence, throughput.

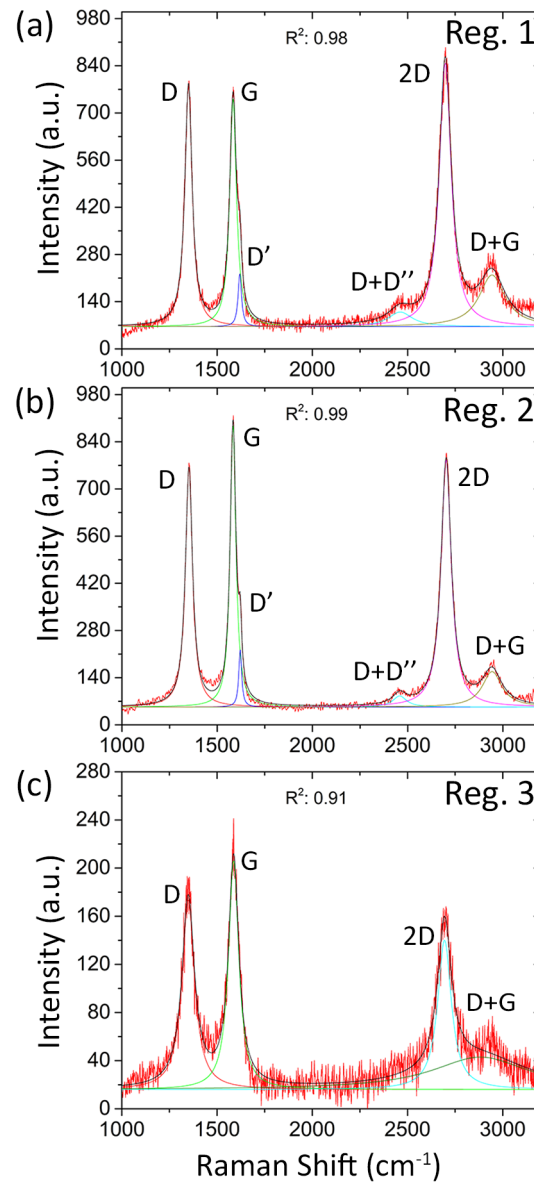


Figure 2.3: Representative Raman spectra of a) Region 1, b) Region 2 and c) Region 3 Laser-induced Graphene material.

Figure 2.3 shows representative Raman spectra from maps taken over samples fabricated with Region 1, 2 and 3 parameters. Table SI-2.6 shows the corresponding Lorentzian fit results. Table SI-2.6 shows the corresponding Lorentzian fit results. For Region 3 material the D' and D+D'' peaks could not be resolved, the D and G peaks are distinctly broader and the I_D/I_G and

I_{2D}/I_G areal peak ratios are smaller than those for Region 1 and Region 2 samples. This suggests increased disorder and defect density in Region 3 material, consistent with the morphology (Figure 2.2f). In early Raman studies of graphite, D' peak signatures were observed in high-quality polycrystalline graphite and also by creating defects in natural graphite single crystals. D' shoulders similar to the data shown in Figure 2.3a,b were observed in polycrystalline graphite with domain sizes (or scattering coherence lengths) ≈ 7 -12 nm. [39,40] The highly intense G peak of Region 1 and Region 2 material, their resolvable D' peak, and sharp D and 2D peaks are suggestive of high-quality graphene-like material with defects present.

Figure 2.4a,b shows fit data (Raman FWHM, peak area as a ratio of the area under the G peak) from 14 random locations for samples from each Region, plotted vs peak position. Spectra from samples fabricated with Region 1 or Region 2 parameters show similar clustering of fit results for the first-order peaks (D, G, D') while Region 3 parameters present a larger distribution of values. This clustering treatment demonstrates that Regions 1 and 2 are similar despite the region 2 material being produced at ~ 5 times the scan speed of the Region 1 material. The larger FWHM(D) values of region 3 indicate significant disorder, in agreement with the observed sample morphology (Figure 2.2e,f).

Detailed Raman spectroscopy studies by Eckmann et al. on exfoliated monolayer graphene with deliberately introduced defects and natural graphite established empirical relationships between the ratios of the D to D' peaks and the nature of the defects: $I(D)/I(D') \sim 13$ for sp^3 defects; $I(D)/I(D') \sim 7$ for vacancy defects and $I(D)/I(D') \sim 3.5$ for boundary defects in natural graphite. [41] Data measured for Region 1 and Region 2 samples showed $I(D)/I(D')$ values between 3.5 and 7 (Figure 2.4c), again consistent with low disorder. The presence of such defects corresponds to the formation process of LIG described in the introduction. The presence of such defects is expected given the LIG formation process: Stone-Wales defects enable the 3D curvature and every pore acts as a series of edge defects. As such, the presence of boundary and vacancy defects is expected and intrinsic to the material. However, it may provide scope for further tuning of laser parameters towards boundary/vacancy dominated defects if it proves to be a desirable parameter.

As LIG is formed *in situ* with the mechanical support of its substrate, it has attracted great

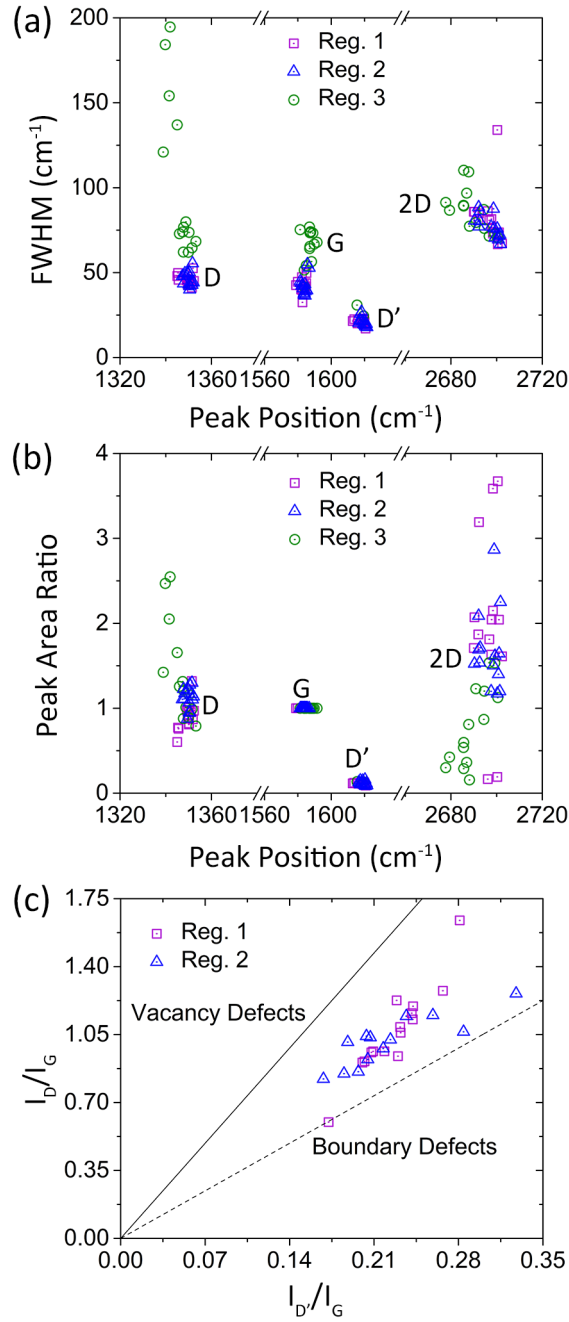


Figure 2.4: a) Full width at half maximum of Raman peaks against their peak position, b) Peak area ratios relative to the G peak against peak position. c) I_D/I_G against $I_{D'}/I_G$ indicative of boundary and vacancy defects.

interest as a gas sensing platform. Sensing devices based on electrical conductivity or thermal conductivity changes in the presence of volatile organic compounds have been reported. [42, 43] The presence of humidity is major challenge for volatile organic compound sensing as water molecules can block sites or lead to spurious responses. Therefore, due to their similarity in observed properties (sheet resistance, morphology, Raman data), both Region 1 and Region 2

laser parameters were used to produce proof of concept LIG humidity sensors. Interdigitated electrode patterns were laser fabricated (Figure 2.5, inset) and functionalized with PVA as a hygroscopic dielectric material to produce capacitive humidity sensors (six devices for each region). Similar exponential capacitive responses were observed for both Region 1 and Region 2 materials with over an order of magnitude increase with increasing relative humidity. Region 1 parameter devices yielded capacitance responses of 0.78 ± 0.04 pF at 0% Relative Humidity (RH), increasing to 31 ± 7 pF at 85.1% RH. Region 2 devices showed comparable responses (0.88 ± 0.04 pF at 0% RH, 28 ± 5 pF at 85.1% RH).

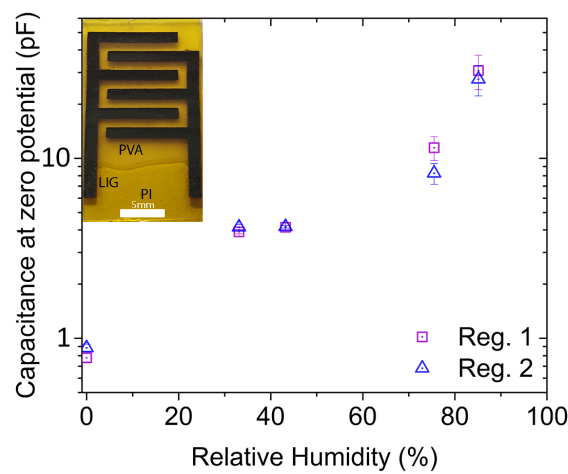


Figure 2.5: Exponential dependence of capacitance at zero potential (2 kHz) on relative humidity for PVA functionalized LIG capacitance humidity sensors produced with Region 1 and 2 conditions. Inset, interdigitated PVA-LIG capacitive humidity sensor.

Measurement of device capacitance vs. exposure time upon switching between different humidity conditions (from 33.3 % to 85.5% RH) yielded Figure SI-2.7. The time taken to reach 90% of the maximum response ($t_{Ads} = 37.5$ mins) was significantly longer than the time taken to return to 90% of the final capacitance ($t_{Des} = 2.0$ mins), suggesting an adsorption barrier energy. This could be addressed in future work through use of thinner films of hygroscopic dielectrics or integration of an external heater to reduce response and recovery times, respectively. [44] The similarity of the resulting humidity sensors highlights the ability of DoE-RS methods to determine potentially useful regions of interest in complex material systems.

Finally, the demonstrated ability of DoE-RS methods to rapidly investigate interactions between factors provides a broad scope for future work in specific device geometry optimizations. Additional factors can be considered, especially the interaction of laser-overlap and multiple

lasing with laser power and scan speed. Many factor interactions are demonstrated in Section SI-2.8 with proof of concept iterative DoE-RS methods using a higher fidelity laser system (Universal Laser Systems PLS 4.75 30W CO₂ 10.6 μm). This laser system allows user control of the laser scan speed and the average laser power (achieved by varying the duty cycle of the electrical modulation waveform). The system also allows user control of the line-line overlap during rastering, the focus height above the sample, the gas flow through the nose cone above the focal plane (nitrogen or air), and the electrically gated modulation rate of the laser along the main raster direction (pixels per inch (PPI)). Screening experiments indicated that the laser modulation rate in the range studied (500-1000 PPI) and gas flow were not significant factors for controlling sheet resistance. A subsequent optimization round highlighted the significance of line-line overlap, both as a main factor and in interactions. As discussed earlier, the multi-pass lasing methods developed by *Tour et al.* [25] revealed the importance of device history effects, including raster beam overlap and laser defocusing. Significant beam overlap between raster lines during patterning and/or multiple-pass lasing can result in LIG formation at reduced dynamic fluence values relative to structures produced by single laser passes, as reported by *Stamatin et al.* The complex, non-linear contributions from key parameters (laser power, scan speed, and beam overlap) highlight the benefits and importance of DoE-RS optimization methods. Where application-specific device geometries are known, further optimization may be possible by considering the raster/vector direction, the beam profile, and time- or history-dependent effects such as thermal relaxation of the substrate between laser passes.

2.5 Conclusion

This work reported the successful use of design of experiment methods in the determination of optima and factor interactions in complex, novel material systems. Iterative DoE processes were demonstrated, realizing both low-sheet resistance and high-scan speed, low-sheet resistance laser-induced graphene. Despite uncertainty in the laser-induced graphene formation mechanism, it was possible to determine these two non-intuitively connected regions possessing similar material properties despite distinct formation conditions. Consequently, all polymer humidity sensors were successfully produced with the LIG materials functionalized with polyvinyl alcohol, displaying equivalent sensitivities. This demonstration of 5x higher throughput speeds highlights the potential of design of experiment methods as an investigative tool.

The employment of design of experiment methods in this work demonstrate not only its efficiency as an optimization strategy but also its use as a rigorous, resource efficient investigation tool. The use of DoE methods allows for appropriate investment of resources at different phases of the process, retaining higher expense experiments, both in analysis time and operational cost for smaller sampling regions and verification processes. This helps to maximize throughput and ensure efficient experimental design. Consequently, regions of interest can be determined rapidly, and time can be spent focusing on high quality, cutting edge work instead of screening steps. For instance, the implementation of in-depth Raman surveys would be impractical on large parameter spaces, while for verification processes their added rigor can be appropriately utilized. This work highlights the importance of such optimization strategies for “all-carbon” sensor elements, where use of metals or other critical raw materials is not favored in order to minimize the environmental footprint and economic costs.

SI-2.1 Design of Experiments Overview

In this work, DoE methods are used as both a rapid optimization method and as an investigative tool; determining the influence of laser parameters on the resulting graphitic material. Unlike traditional OFAT experimental processes, DoE allows for the consideration of all factors influencing a process and its measurable outputs systematically and simultaneously. Combinations of high and low levels of the factors under study are utilized; reducing the total number of samples needed and allowing the investigation of interactions between factors. Statistical analysis methods such as ANOVA are used to determine statistically significant factors through consideration of F-scores.

The selection of factors is critical as each unnecessary factor increases the number of samples required; although less than an equivalent OFAT investigation. If many factors are of interest, the dominant factors and significant interactions can be determined in an initial screening fractional-factorial experiment. Which provides insight into multiple factors with reduced experimental cost; although with reduced accuracy, by sampling a subset of a standard DoE of all the initial factors. Reduction in spurious factors, minimizes the number of samples needed in later stages through low experimental cost investigations. This benefit is compounded if initial investigations utilize lower precision-high throughput methods and retains higher precision methods for subsequent rounds of optimization or verification. The enhanced precision of higher experimental cost methods can thus be decoupled from every stage of the optimization procedure, while still retaining statistical significance.

The ANOVA methodology of DoE monitors the influence of factors above the background of variance in the responses. Allowing for the determination of which factors, or combination of factors, contributes to the change in response variables, above the innate variability in those measurements. Reducing the underlying variability is therefore key in observing significant effects. DoE methods require several steps to avoid instrumental drift or user influence impacting the results. The most fundamental of these is randomization of run order of different factor level combinations in both fabrication and measurement, to avoid equipment drift over the course of

experimentation confounding intrinsic effects. Thereby any influence that sample run order has on the model can be observed and eliminated.

However, pure randomization of run order isn't always viable as some "hard to change" factors, may be difficult to change from one run to the next. Instead a method called blocking is employed whereby runs at the same level of that hard to change factor are formed into a subset of the overall experiment. Additional verification points are necessary in each block to account for the reduced randomness in the run order. The influence of the hard to change factor on the variability can therefore be minimized. Hard to change factors can also be financially limiting factors such as expensive substrates. DoE methods can therefore be used to tailor a statistically robust methodology around resource and time constrained situations.

Beyond looking at only the direct linear influence of each factor on each of the responses as one would with OFAT methods; DoE also considers the interaction of each factor with every other factor on each response. This allows for non-intuitive response combinations to be considered that would not be easily determinable through OFAT methods; at no additional experimental cost. This is of interest in novel or complex systems. The set of significant main- and interaction-factors defines a model predictive of the behavior of the responses. This would provide greater insight into the factor-response relationship and allow for the most significant factors and facilitate their rapid optimization.

Although any arbitrary order of factor or factor-interactions can be considered under DoE methods by finding the products of the measured responses to produce a novel response factor, it is necessary to avoid over-fitting the data set. It is also critical to avoid introducing factors whose influence cannot be discerned from other factors. In other words, the smallest set of discretely understandable factors should be considered. Two factors are considered confounded when their combination of high and low levels for each run are the same.

Table SI-2.1 displays a sample of full 3 factor (A,B,C) two level-factorial design, where "+" denotes the High level for the factor and "-" the low level. As the encoded levels for each factor and interaction of factors considered are discrete, each can be considered without being confused for another factor. Table SI-2.2, a half fractional subset of Table SI-2.1, displays a confounded relationship between main factor B and interaction factor AC. As such, it is uncertain if the

influence on a response is due to either factor B or the interaction of factors A and C, when using the half fractional design. This is a limitation of fractional designs as even low order interaction effects can become confounded with main effects. Hence why fractional designs are normally used as a screening process to reduce the total number of factors. As when used as a principle tool with few factors they can be unable to fully encapsulate interactions or high order dependences. Similarly, high order factors and interactions become confounded for even full factorial designs.

When considering which factors to include in a model of the DoE responses, the following must be considered: Do not include higher order factors/interactions that confound with a lower order factor. Select factors based on their significance as verified by ANOVA. If any higher orders of a given factor are included then the interaction factors below that order should also be included in the model, to account for model hierarchy, even if they are not statistically significant i.e. a factor of A^3 would then require A^2B to be included in the model even if it was not significant in its own right.

Table SI-2.1: Example full two factorial DoE design. “+” indicates a “high” level and “-“ a “low” level.

Run	1	2	3	4	5	6	7	8
A	+	-	-	+	+	-	+	-
B	-	+	-	+	-	+	+	-
C	-	-	+	-	+	+	+	-
AB	-	-	+	+	-	-	-	+

Table SI-2.2: Example Half-fraction two factorial DoE design, demonstrating confounding. “+” indicates a “high” level and “-“ a “low” level.

Run	1	2	3	7
A	+	-	-	+
B	-	+	-	+
C	-	-	+	+
AB	-	+	-	+

These standard DoE methods are often sufficient for initial studies. A more generalized method is also possible; response surfaces. Instead of combinations of just high and low levels of factors additional central and edge points are considered. Although the underlying methodology is the same; significant factors and interactions are found through ANOVA and a model is formed

as would be the case for a traditional two level-factorial DoE. The model for the responses is normally viewed as a response surface and can be used to predict optima and provide insight into complex factor interactions. When numerous responses are involved, or if the optimization relative to an underlying factor is desired conditional optimization can also be carried out. The response surface method also allows for more complex factor orders and interactions to be included without confounding.

As outlined here, DoE methods have many benefits. These include resource efficient optimization, statically verifiable decision making and increased insight into process behavior. As such its implementation as a path finding tool using low experimental cost response factors followed by increasingly refined measurement methodologies reflective of the increased robustness of the optimization process, allows for low resource wastage while ensuring comprehensive analysis.

SI-2.2 Design of Experiments Iterations

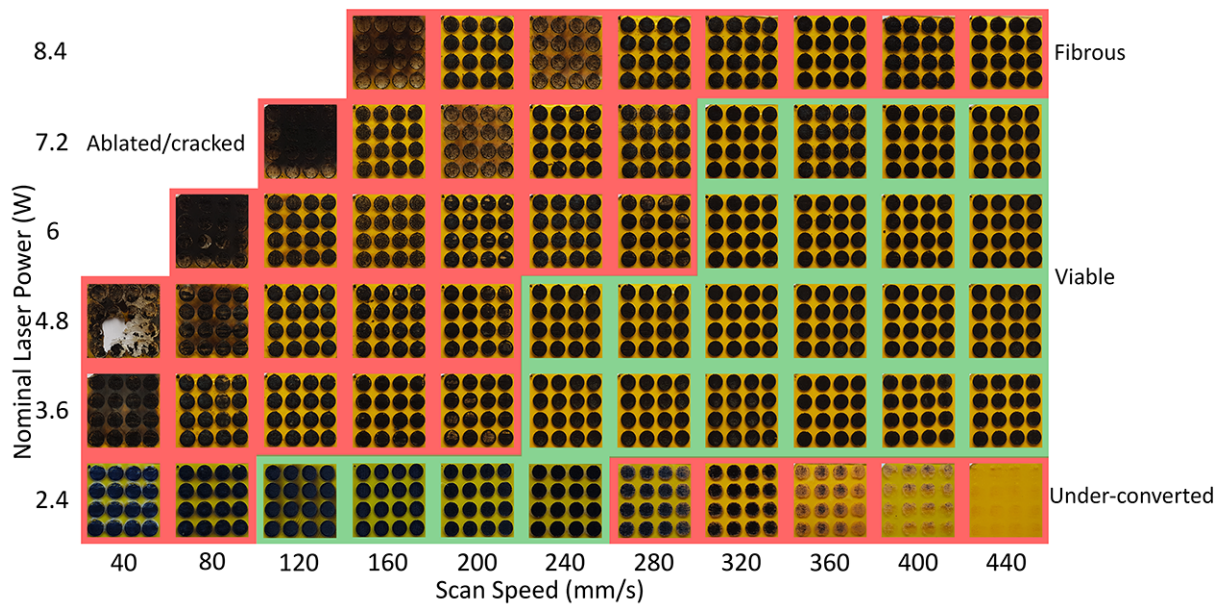


Figure SI-2.1: Initial visual inspection DoE investigation vs scan speed and laser power.

Three Regimes were observed:

1. Fibrous material with high aspect ratio fibres (Red-bordered photos in Figure SI-2.1)
2. Visibly defective samples/incompletely converted samples which either had ablated material away or had insufficiently patterned the LIG (Red-bordered photos in Figure SI-2.1)
3. Homogeneous black materials with no visible defects (Green-bordered photos in Figure SI-2.1).

The resulting map of visually inspected samples was produced as shown in Figure SI-2.1. The region of viable samples was used to define an initial DoE-RS experiment. Qualitative measurements on a scale of [1-10] were made for each visual response (Fibrosity, Redeposited Residue and Damage). The resulting response surfaces indicated that more desirable samples (low fibrosity, low residue, low damage) samples could be achieved at lower laser power, and higher scan speed. The interplay of these factors can be seen in their respective response plots whereby bands of equivalency are predicted (Figure SI-2.2). These predictions call for non-intuitive combinations of laser power and scan speed and vary from response to response.

Following from the prediction of the initial DoE-RS, to focus on lower laser powers and higher scan speeds as shown to be more desirable, a further DoE-RS was constructed taking the higher scan speeds and lower laser powers of the initial DoE-RS as its region of interest. The higher desirability region (200-440 mm/s, 2.4-5.4 W) determined from the initial DoE-RS was selected for a subsequent sheet resistance DoE-RS (Figure SI-2.3). The resulting response surface predicts a region of interest at low-laser power and moderate scan speed that tapers as with increasing laser power and scan speed. With this tapering there is a predicted increase in sheet resistance. To either side of this region are parameters of high sheet resistance that quickly fall off into non-continuous or damaged sampling conditions. As such a subsequent DoE-RS process investigating both the higher scan speed, moderate sheet resistance and the global minima regions were not possible without requiring the production of non-viable samples. The low sheet resistance region was selected for further investigation, expanding the parameter space to lower scan speeds and laser powers to find the global minimum. This was necessary as the predicted behavior was for sheet resistance to decrease as both laser power and scan speed decreased in the initial sheet resistance DoE-RS.

The resulting response surface is that presented in Figure 2.1d using sampling points shown in Table SI-2.3. The resulting response surface is complex. The regions to either side are known to be non-viable regions with damaged/under-converted material and as such it would be expected that they would have larger sheet resistance values. Similarly, based off the first electrical DoE-RS saddle point, it was expected that the sheet resistance should decrease with decreasing laser power and scan speed. This was observed globally in this design, although a region of significantly higher than anticipated sheet resistance was predicted.

Based on the design it is seen that the two-factor interactions and fifth order interactions are seen to hold significance. The sixth order interactions could not be considered as they are confounded with other interactions. Consequently, interactions up to the fifth order have been considered for the model Table SI-2.4. It was seen that the B^5 term was not significant and as such was neglected from the model. Although, several of the interaction terms considered in the model on their own are not supported by statistical significance such as A^2B , these terms are required to maintain the hierarchy of the model, Table SI-2.5. The model was shown to be

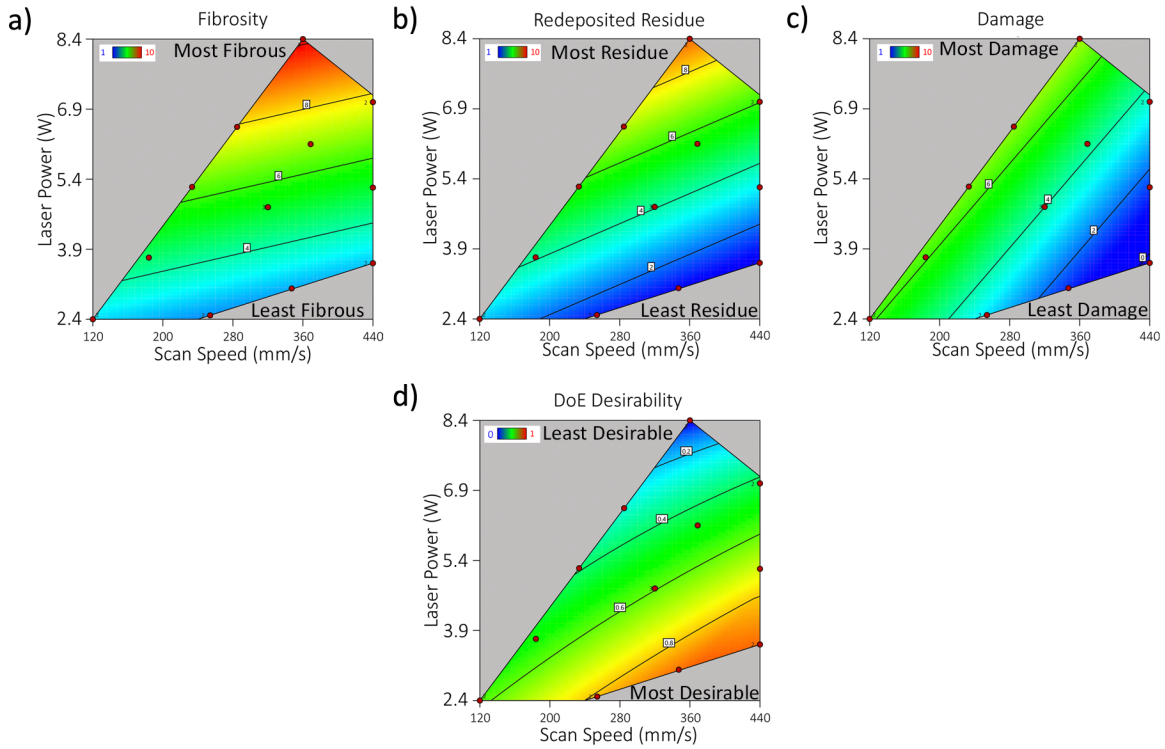


Figure SI-2.2: Initial qualitative DoE response surfaces produced from visual inspection scores. a) Conditionally optimized DoE desirability for minimized fibrosity, minimized redeposited and damage; b) Response surface for visually inspection graded fibrosity; c) Response surface for visually inspection graded redeposited residue; d) Response surface for visually inspection graded sample damage.

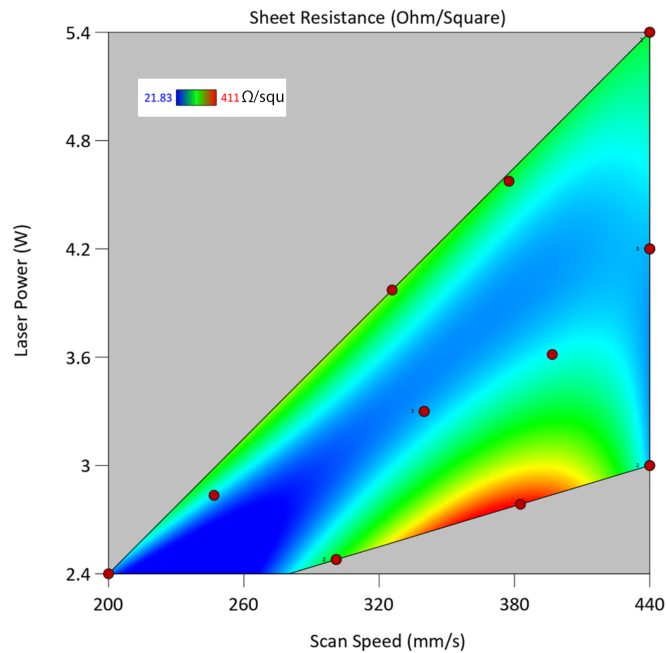


Figure SI-2.3: Initial 18-point electrical DoE response surface indicating, in blue, two regions of predicted lower sheet resistance for further investigation.

statistically significant with a p-value < 0.0001, the residual lack of fit was insignificant with a p-value of 0.44. This suggests good confidence in the selected model.

Table SI-2.3: Randomized experimental run order and sheet resistance response.

Run	Scan Speed (mm/s)	Laser Power (W)	Sheet Res. $\Omega/Squ.$	Run	Scan Speed (mm/s)	Laser Power (W)	Sheet Res. $\Omega/Squ.$
1	340	3.45	27.8	16	340	3.39	29.1
2	278	2.96	29.6	17	189	2.58	373.5
3	340	3.00	33.1	18	270	3.45	27.2
4	150	2.25	33.1	19	189	2.58	383.6
5	227	3.18	26.1	20	60	1.95	27.4
6	254	2.58	130.7	21	340	3.27	30.7
7	340	3.45	34.7	22	340	3.06	229.7
8	80	1.98	82.8	23	155	2.16	64.9
9	220	2.85	440.5	24	191	2.94	104.5
10	340	3.00	40.1	25	170	2.22	62.8
11	55	2.10	15.5	26	55	2.10	18.0
12	180	2.76	81.5	27	264	3.33	37.2
13	121	2.52	662	28	157	2.19	288.1
14	119	2.19	23.4	29	165	2.19	123.5
15	55	2.10	15.5	30	297	3.27	39.7

Table SI-2.4: Fit summary for different response orders. Suggesting that a fifth order model is statistically significant.

Source	Sequential p-values	Lack of Fit p-value	Adjusted R ²	
Linear	0.2301	0.0015	0.0367	
2FI	<0.0001	0.0057	0.4531	
Quadratic	0.2266	0.0061	0.4765	
Cubic	0.1659	0.0076	0.5390	
Quartic	0.0083	0.0305	0.7627	
Fifth	0.0036	0.3637	0.9366	Suggested
Sixth	0.3637		0.9455	Aliased

Traditional OFAT methods would not easily be able to predict the behaviors seen, whereby non-intuitive interactions of laser power and sheet resistance result in complex response surfaces. Additional factors could be considered in this way, such as; laser defocusing, gas environment, support substrate variation, polyimide thickness and polyimide formulations. These, and other potential features could be examined in through a similar DoE process, or through half-factorial methods to further define key factors in LIG formation and, like with what was shown for laser power and scan speed determine, non-intuitive interactions.

Figure SI-2.4 presents diagnostic plots for the DoE response surface presented in Fig. 2.1d. No anomalous results are present except for a high leverage point as noted by the large Cook's distance. This corresponds to 270 mm/s, 3.45 W, a corner point of the design, suggesting that this point has a larger than normal impact on the design. In future works, additional points would be incorporated near that point. Despite this point of high leverage, the diagnostics suggest confidence in the design used.

Table SI-2.5: Analysis of Variation outputs for model constituents at 95% confidence level.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0097	19	0.0005	25.46	<0.0001	Significant
A-Scan Speed	0.0001	1	0.0001	3.02	0.1129	Insignificant
B-Laser Power	0.0001	1	0.0003	3.00	0.1137	Insignificant
AB	0.0003	1	0.0004	13.47	0.0043	Significant
A2	0.0004	1	0.0003	19.91	0.0012	Significant
B2	0.0003	1	0.0000	16.95	0.0021	Significant
A2B	0.000	1	0.0000	16.95	0.0021	Significant
AB2	0.0000	1	0.0000	1.00	0.3405	Insignificant
A3	0.0000	1	0.0000	1.97	0.1903	Insignificant
B3	6.633E-6	1	66.63E-6	0.33	0.5778	Insignificant
A2B2	0.0003	1	0.0003	15.34	0.0029	Significant
A3B	0.0004	1	0.0004	19.06	0.0014	Significant
AB3	0.0002	1	0.0003	11.86	0.0063	Significant
A4	0.0004	1	0.0004	22.37	0.0008	Significant
B4	0.0002	1	0.0002	10.89	0.0080	Significant
A3B2	0.0005	1	0.0005	26.94	0.0004	Significant
A2B3	0.0005	1	0.0005	22.63	0.0008	Significant
A4B	0.0006	1	0.0006	29.95	0.0003	Significant
AB4	0.0004	1	0.0004	18.13	0.0017	Significant
A5	0.0006	1	0.0006	30.02	0.0003	Significant
Residual	0.0002	10	0.00002			
Lack of Fit	0.0001	5	0.00002	1.15	0.4393	Insignificant
Pure Error	0.0001	5	0.00002			
Corr Total	0.0099	29				

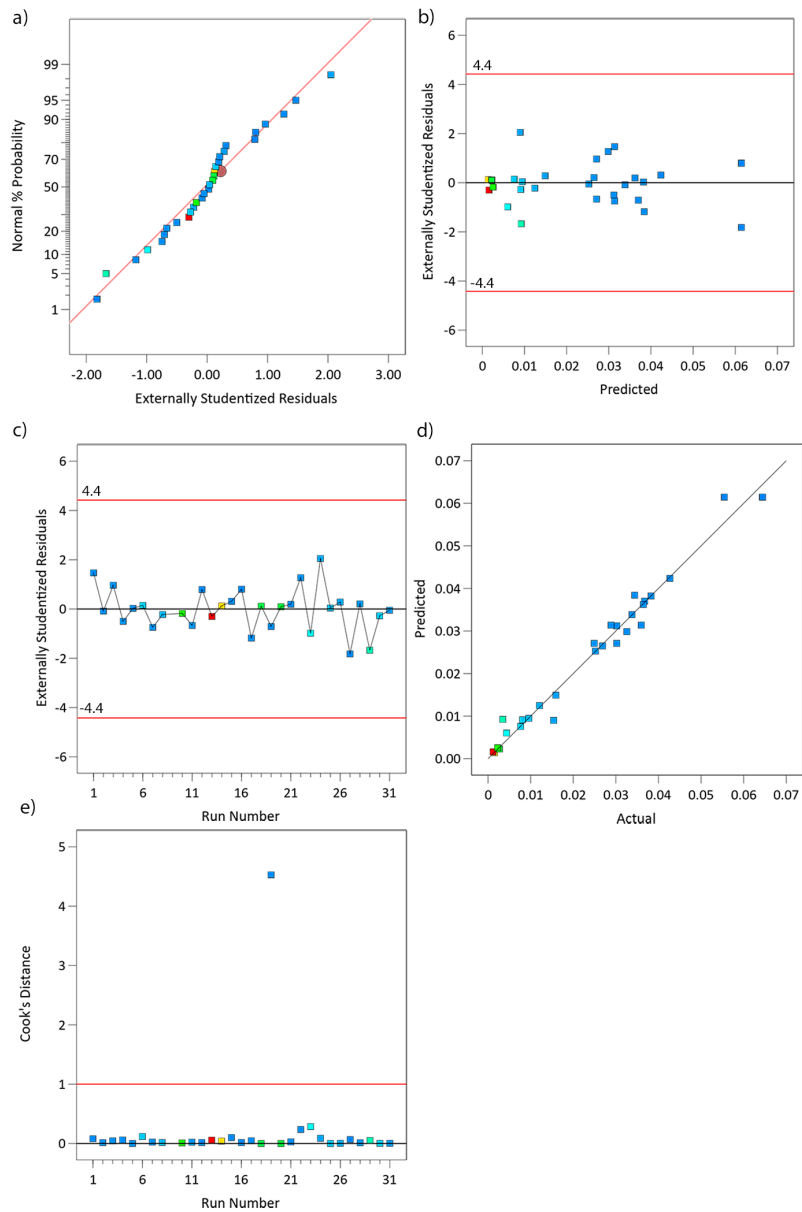


Figure SI-2.4: Diagnostic tests to ensure the validity of application of ANOVA and DoE optimization. a). Normal % Probability against Externally studentized residuals indicating normality of transformed dataset, b). Plot of externally studentized residuals against predicted values indicating that there is no propagating trend in the prediction, c). Externally studentized residuals against sample run order indicating no experimental bias due to run order, d). Plot of predicted sheet resistance values against actual values with a superimposed line of slope one, indicative of experimental results corresponding to a low bias regime e). Plot of Cook's distance against sample run order indicating a point of high leverage: (270 mm/s, 3.45 W).

SI-2.3 Raman Results

Table SI-2.6: Representative Raman characterization of Region 1, 2 and 3 samples.

Region	Pos. (cm^{-1})	D FWHM (cm^{-1})	G Pos (cm^{-1})	G FWHM (cm^{-1})	2D Pos. (cm^{-1})	2D FWHM (cm^{-1})	I_D/I_G	I_{2D}/I_G	aR^2
1	1345	50	1580	45	2690	86	1.3	2.1	0.99
2	1352	46	1583	37	2702	65	1.1	1.6	0.99
3	1349	80	1587	65	2694	87	1.0	0.9	0.91

SI-2.4 Electrical Characterisation Modified Method

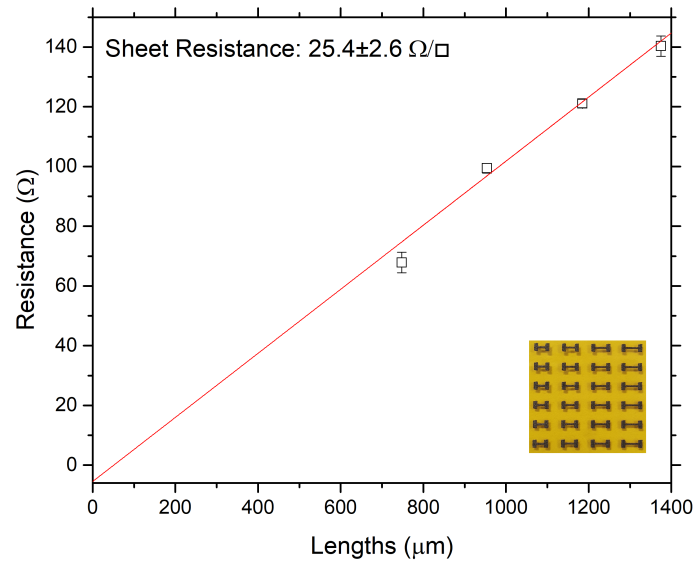


Figure SI-2.5: Sheet resistance plot recorded using standard TLM methods on Region 1 material parameters found using the mm-scale dumbbell test structures. The intercept was found to be $-5.4 \pm 12.1 \Omega$.

Early experiments used "dumbbell" structures, it was observed that the sheet resistance was the dominant factor. This can be seen Fig SI-2.5, whereby the intercept is approximately zero. Consequently to reduce the sampling time later optimization used cm-scale rectangular bars (2×20 mm) structures where the large aspect ratio minimised the influence of contact resistance, requiring fewer measurements.

SI-2.5 Additional SEM Imagery

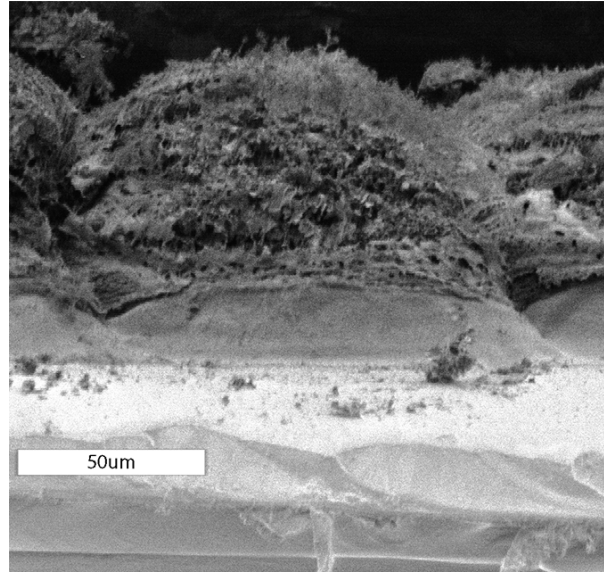


Figure SI-2.6: Cross-sectional SEM image of Region 1 parameter LIG of thickness $50\ \mu\text{m}$.

SI-2.6 Proof of Concept Humidity Sensing: Time Constants

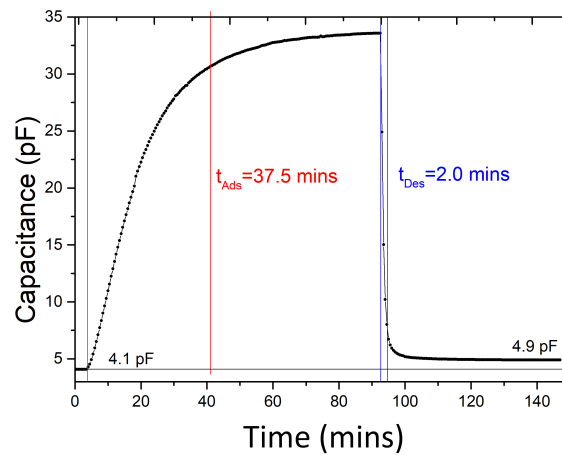


Figure SI-2.7: Humidity switching behavior of Region 1 PVA functionalized LIG being switched between a 33.3% to 85.1% relative humidity environment. The red demarcations indicate the time taken to reach 90% of the maximum value of capacitance recorded. The blue demarcations indicate the time taken to reach 90% of the minimum recovered capacitance value.

SI-2.7 Beam Overlap Estimates (HQ-3020B Laser)

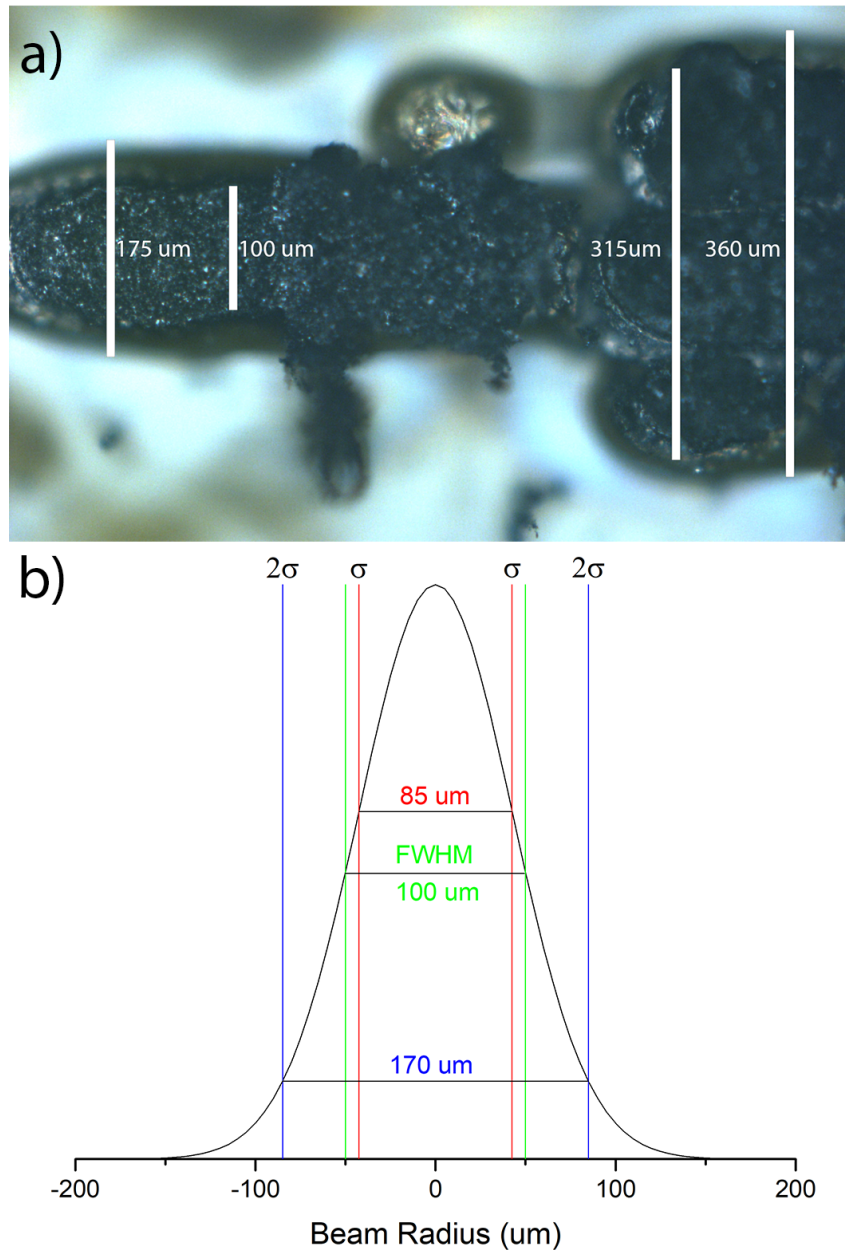


Figure SI-2.8: a) Optical microscope image of LIG on LIG with single and multi-line regions. b) Estimated laser beam profile from microscope image and Equations SI-2.1, SI-2.2.

For the low-cost laser system used in this work, the laser beam profile was not well defined, nor could the overlap between raster lines be selected. To estimate these values a tapered pattern was produced using Region 1 parameters to achieve a single line region connected to a multi-line rastered region. Optical images (Zeiss Auxioscope, 10 $\times$ objective) were recorded and are presented in Figure SI-2.8. In the single pass region the graphitised material is of diameter ~ 100

μm , while the total width of the region modified by the laser is $\sim 175 \mu\text{m}$. The multiple-line region contains three lines of graphitic material within $315 \mu\text{m}$ but has had an observable effect on $360 \mu\text{m}$ of polyimide substrate. The altered, but un-graphitized material, is ascribed to polyimide that has been partially modified by laser irradiation of insufficient fluence to achieve conversion. Consequently, if the beam profile is assumed to be Gaussian and the FWHM of that profile taken as $100 \mu\text{m}$, the width of the converted region of a single pass, then the beam diameter at 2σ is $170 \mu\text{m}$. This is quite close to the observed outer estimates for influenced but unconverted polyimide.

Given the beam diameter of $170 \mu\text{m}$ then from the optical image outer dimension for the three channel region the overlap can be estimated from:

$$W_{Total} = nw_1 - (n - 1)a \quad (\text{SI-2.1})$$

$$a = (W_{Total} - nw_1)/(1 - n) \quad (\text{SI-2.2})$$

Where n is the number of raster lines, W_{Total} is the width of the n channels together, w_1 is the width of a single channel and a is the overlap of channels.

Therefore, the overlap is $\approx 85 \mu\text{m}$. This is largely the lower intensity portion of the beam profile. It has been previously noted by *Chyan et al.* that overlaps of multiple lasing processes can produce LIG at fluences below that required in a single pass [25].

SI-2.8 Multi-Parameter DoE Optimisation (PLS Laser)

Initial works demonstrated here using a hobbyist CO₂ laser system highlight the great potential of DoE methodologies for complex material investigation processes. Subsequently, a Universal Laser Systems PLS 4.75 CW CO₂ laser system (30 W, 10.6 μm , with a Gaussian beam profile (close to TEM₀₀) with quoted M² value of 1.3 ± 0.2) has been used to convert polyimide into LIG while varying:

- Average Laser Power (14-20% duty cycle of 30 W max power)
- Scan Speed (10-18%, for mm/s values, see estimated calibration curve, Figure SI-2.9)
- Laser Focus (in focus -0.26mm to below focal plane 0.00 mm, see Figure SI-2.10)
- Modulation of RF energy to laser plasma “Pulses” per inch (500-1000 PPI), estimated temporal frequency $\sim$ kHz for this work
- Image Density (line density and raster beam overlap 1-7, see Figures SI-2.11-SI-2.12)
- Gas flow (nitrogen or air)

This laser allows control over more parameters than the HQ-3020B laser. The Pulses per inch is the repetition rate of the laser along the direction of the raster line. Image Density determines the number of raster lines used to produce the pattern – a measure of beam overlap. Focus can be altered by raising/lowering the platen of the laser bed above/below the focused point of -0.26 mm for polyimide covered glass slides. Moving below -0.26 mm towards 0 mm would defocus the beam, causing it to broaden. This laser allows for controlled gas flow during laser operation to prevent damage to the laser optics – the composition of the gas can be varied.

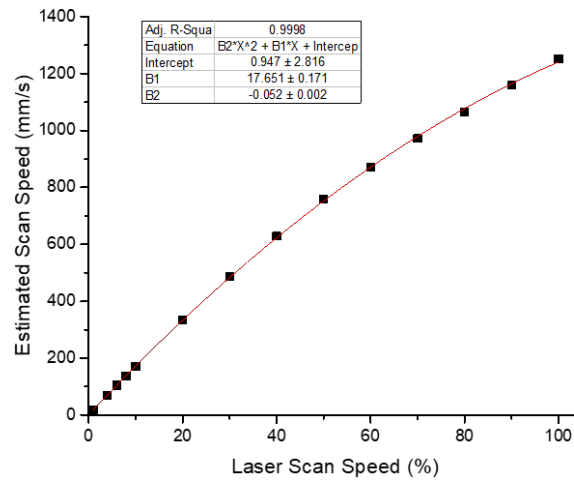


Figure SI-2.9: Scan speed calibration curve for ULS PLS 4.75 10.6 μm CO₂ laser engraver.

Figures SI-2.11 & SI-2.12 show optical micrographs of samples fabricated using Image Density settings ranging from ID 1 to ID 7. This demonstrates the monotonically increasing line density used. At the lowest Image Density setting (ID1), parallel lines of separate LIG are produced, while for Image Density settings of ID 3 and higher, there is clear overlap of individual line paths. The degree of overlap increases until at ID 7, where it becomes difficult to deconvolute the lines.

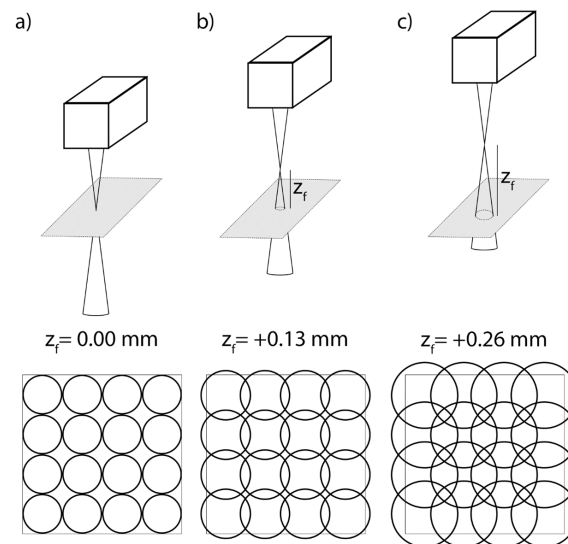


Figure SI-2.10: Schematic displaying laser overlap caused by moving sample plane below focal plane of laser head, a) in focus, b) nominally below focal plane, c) far beyond focal plane. Note: $z_f = z + 0.26 \text{ mm}$.

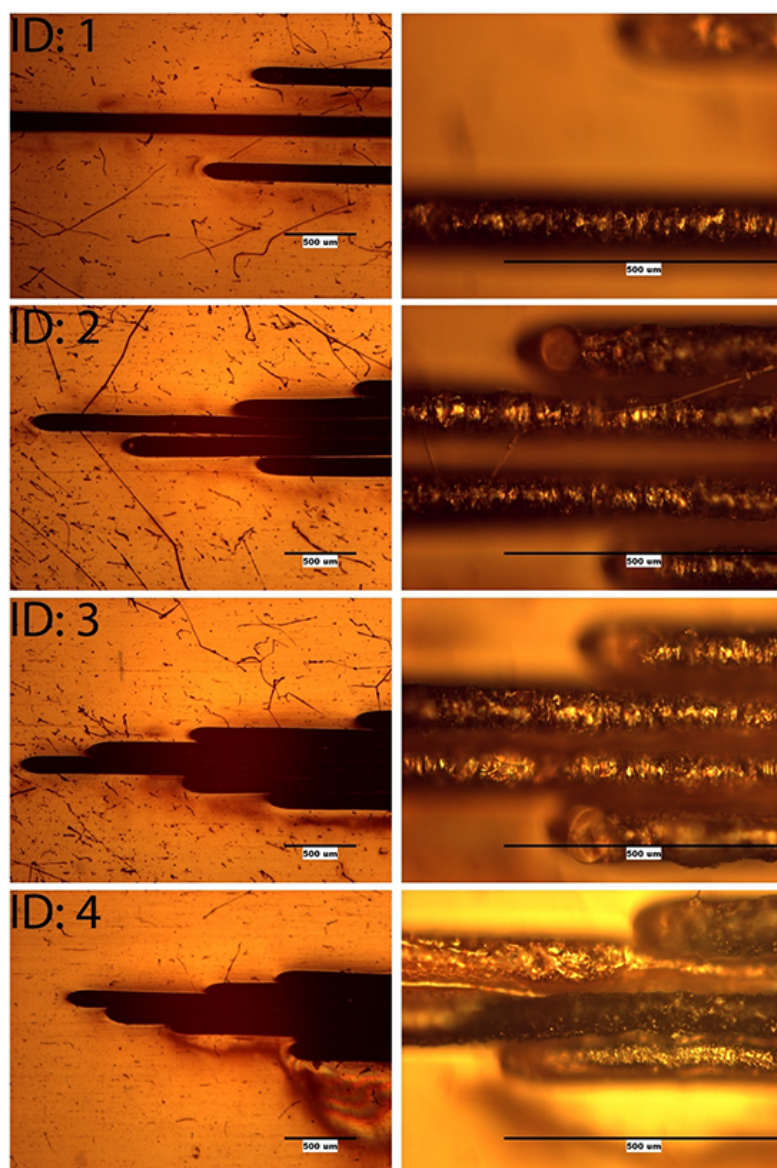


Figure SI-2.11: Optical micrographs of laser-induced graphene samples produced at identical laser parameter but varying Image Density 1-4.

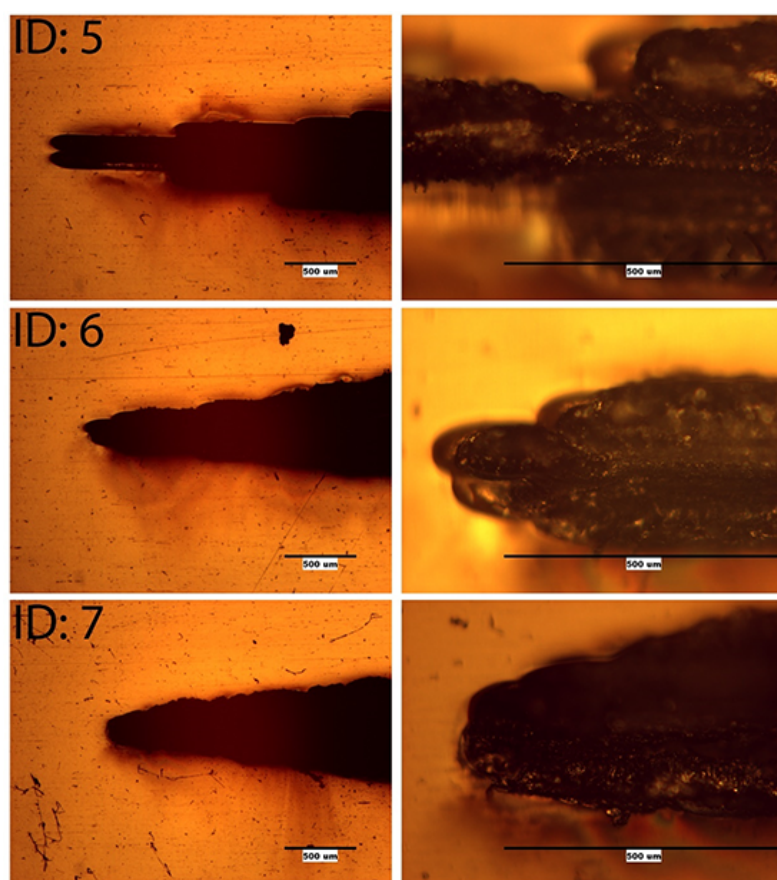


Figure SI-2.12: Optical micrographs of laser-induced graphene samples produced at identical laser parameter but varying Image Density 5-7.

SI-2.8.1 Multi-parameter DoE Screening Experiments

The initial Split-Plot Central Composite Design (Table SI-2.7) was analysed. The model showed that Gas Flow type and Pulses per Inch (in the 500-1000 PPI range) were not statistically significant factors and were therefore rejected from the model. Figure SI-2.13 shows screening experiment model for the significant factors: Laser Power, Scan Speed, Image Density and Focus.

This initial screening experiment demonstrates, not only the insignificance of the Pulses per inch and Gas flow type factors, but also demonstrates that sheet resistance, the response factor, decreases with increasing laser power and image density, it also increases with increasing scan speed and as the laser is defocused. **Interactions between factors are not captured in this level of experiment** as excessive number of experiments would be required to capture their influence without first screening for significant factors. This central composite design informs another round of investigation focusing not only on the four significant factors but allowing for the consideration of interaction effects and quadratic dependences on factors, SI-2.8.

The subsequent round of DoE also further restricted the limits of scan speed and image density to ensure viable sampling conditions. Higher scan speeds and lower image densities prevented the formation of under-written LIG samples that would not be contactable or would produce widely spaced LIG pathways that act as independent parallel paths for conduction. This modification reduced the observed sheet resistance values compared to the first round, as extreme values such as low laser power-high scan speed - low image density would no longer confound and produce highly resistive material. Consequently, due to the restricted domain, selecting for usable sampling conditions a revised model of factors was generated.

The revised model was analysed and the expected reduction in extreme values achieved, as demonstrated in Figure SI-2.14. The model also observed that the Laser Power – Image Density and Scan speed – Image Density interactions were present and statistically significant. Further, (Image Density)² proved to be a statistically significant factor. The U-shaped quadratic dependence on Image Density, indicates the fundamental importance of the line-line overlap in LIG formation. If they are too widely spaced, the sheet resistance increase; if they overlap too much, damage occurs to the initial material. High-quality LIG needs a balance between

multi-lasing and ablation of previously formed material.

High-quality LIG has many controlling factors, the complexity of which is shown in Figure SI-2.15 whereby multiple complex interactions between factors are demonstrated. One-factor-at-a-time experimental methods would struggle to account for these relationships in resource efficient optimisation processes. However, DoE methods have allowed for the screening of spurious factors and initial insight into a highly interdependent parameter space requiring only 52 samples to be produced and tested. This demonstrates the valuable transferable nature of DoE optimisation, both between laser systems for LIG formation, and lays out a clear framework for using DoE as part of a resource efficient investigation strategy.

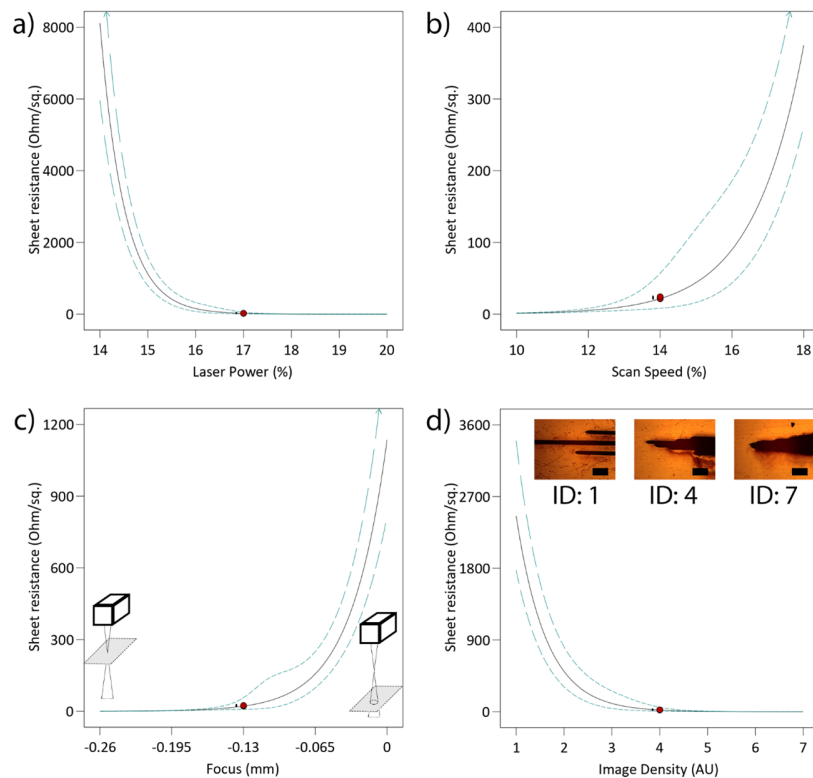


Figure SI-2.13: Initial screening experiment predicted sheet resistance responses for a) Laser Power, b) Scan Speed, c) Focus (inset: schematics depicting focal planes), d) Image density (inset: patterns at image densities 1, 4 and 7, scale bar: 500 μm).

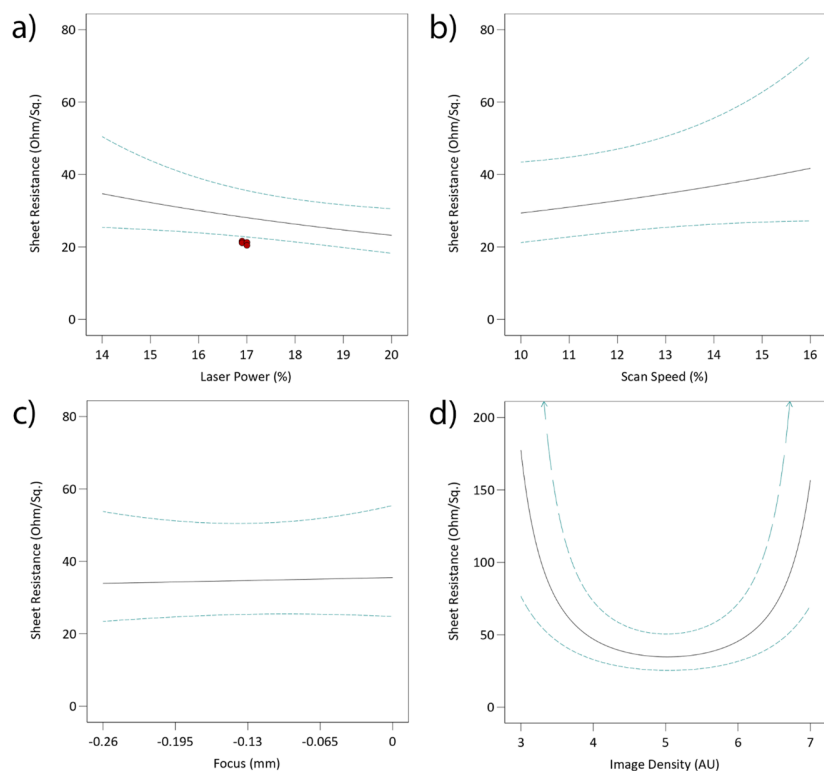


Figure SI-2.14: Initial screening experiment predicted sheet resistance responses for a) Laser Power, b) Scan Speed, c) Focus (inset: schematics depicting focal planes), d) Image density (inset: patterns at image densities 1, 4 and 7, scale bar: 500 μm).

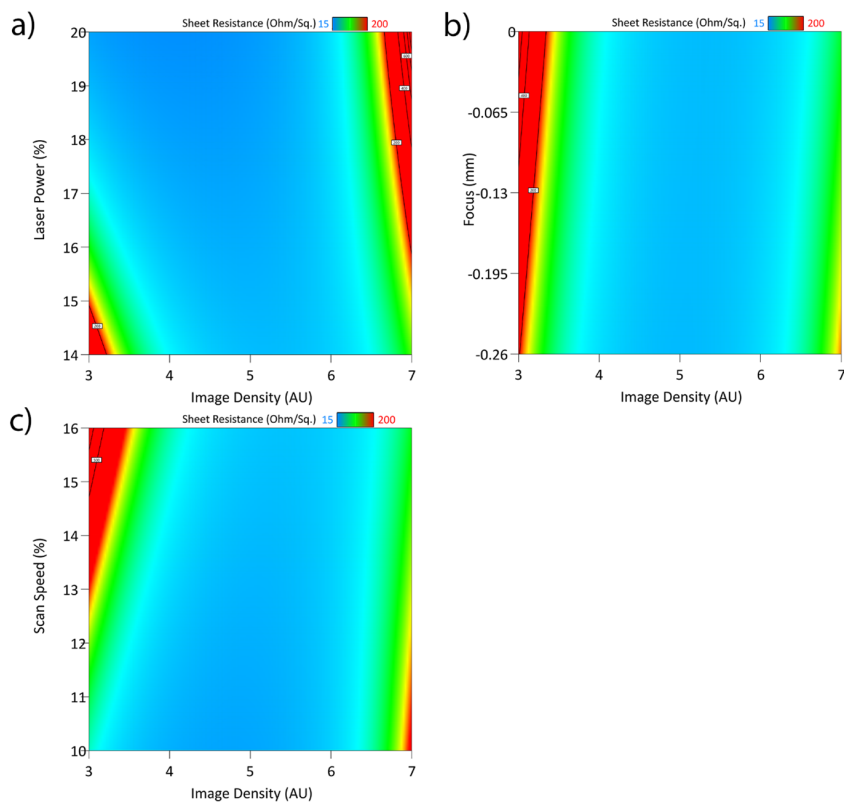


Figure SI-2.15: Contour Plots displaying interaction effects between factors and Image Density, a) Laser Power, b) Focus and c) Scan Speed.

Table SI-2.7: 6-factor Split-plot Central Composite Design Response Surface with Focus as a Hard-to-change factor

Block	Run	Laser Power	Scan Speed	PPI	Image Density	Focus	Gas Flow	Sheet Res.
1	1	17	14	750	4	-0.13	N ₂	23
1	2	17	14	750	4	-0.13	N ₂	28
1	3	17	14	750	4	-0.13	N ₂	21
1	4	17	14	750	4	-0.13	N ₂	21
1	5	17	14	750	4	-0.13	Air	22
1	6	17	14	750	4	-0.13	Air	21
1	7	17	14	750	4	-0.13	Air	22
1	8	17	14	750	4	-0.13	Air	24
1	9	17	14	750	4	-0.13	Air	24
2	10	17	14	750	4	-0.13	N ₂	24
2	11	17	14	750	4	-0.13	N ₂	24
2	12	17	14	750	4	-0.13	N ₂	24
2	13	17	14	750	4	-0.13	N ₂	21
2	14	20	10	1000	1	0	N ₂	16
2	15	14	10	1000	7	0	Air	186
2	16	14	10	500	1	-0.26	Air	186
2	17	14	18	1000	7	-0.26	N ₂	746
2	18	17	14	750	4	-0.13	Air	24
2	19	17	14	750	4	-0.13	Air	23
2	20	17	14	750	4	-0.13	Air	23
2	21	14	10	500	7	0	Air	177
2	22	20	18	1000	1	0	Air	5000

Table SI-2.8: 4-factor Central Composite Design Response Surface with Focus as a Hard-to-change factor.

Run	Laser Power (%)	Scan Speed (%)	Focus (mm)	Image Density (AU)	Sheet Res. (Ohm/Sq.)
1	17	10	-0.12	5	61
2	16.9	13	-0.14	5	21
3	17	14	-0.26	3	52
4	14	10	0.00	5	18
5	20	12	-0.26	5	20
6	18.9	14	-0.08	3	25
7	18.4	16	-0.26	7	767
8	20	16	0.00	5	25
9	14	12	-0.12	3	88
10	20	11	0.00	3	19
11	20	12	-0.26	5	19
12	16.4	12	0.00	7	313
13	20	16	-0.19	3	29
14	16.9	13	-0.13	5	21
15	17.5	12	-0.23	7	620
16	17	13	-0.13	5	21
17	17	10	-0.12	5	53
18	20	14	0.00	7	430
19	16.7	10	-0.26	3	18
20	14	16	-0.07	7	82
21	14	12	-0.11	3	83
22	14	16	-0.07	7	72
23	14	14	-0.26	4	58
24	14	11	-0.26	7	140
25	16.9	13	-0.13	5	22
26	15.6	63	0.00	3	1000
27	20	10	-0.14	7	337
28	20	10	-0.17	3	16
29	17	13	-0.13	5	21
30	16.8	12	0.00	4	23

BIBLIOGRAPHY

- [1] K. Bolotin, K. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. Stormer, “Ultrahigh electron mobility in suspended graphene,” *Solid State Communications*, vol. 146, p. 351–355, Jun 2008.
- [2] G. Chen, Y. Liu, F. Liu, and X. Zhang, “Fabrication of three-dimensional graphene foam with high electrical conductivity and large adsorption capability,” *Applied Surface Science*, vol. 311, p. 808–815, Aug 2014.
- [3] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, “Superior thermal conductivity of single-layer graphene,” *Nano Letters*, vol. 8, no. 3, p. 902–907, 2008.
- [4] C. Lee, X. Wei, J. W. Kysar, and J. Hone, “Measurement of the elastic properties and intrinsic strength of monolayer graphene,” *Science (New York, N.Y.)*, vol. 321, p. 385–8, Jul 2008.
- [5] I. Meric, M. Y. Han, A. F. Young, B. Ozyilmaz, P. Kim, and K. L. Shepard, “Current saturation in zero-bandgap, top-gated graphene field-effect transistors,” *Nature Nanotechnology*, vol. 3, p. 654–659, Nov 2008.
- [6] J. Xia, F. Chen, J. Li, and N. Tao, “Measurement of the quantum capacitance of graphene,” *Nature Nanotechnology*, vol. 4, p. 505–509, Aug 2009.
- [7] X. Du, I. Skachko, A. Barker, and E. Y. Andrei, “Approaching ballistic transport in suspended graphene,” *Nature Nanotechnology*, vol. 3, no. 8, p. 491–495, 2008.
- [8] R. Murali, K. Brenner, Y. Yang, T. Beck, and J. D. Meindl, “Resistivity of graphene nanoribbon interconnects,” *IEEE Electron Device Letters*, vol. 30, p. 611–613, Jun 2009.
- [9] V. B. Mohan, K.-t. Lau, D. Hui, and D. Bhattacharyya, “Graphene-based materials and their composites: A review on production, applications and product limitations,” *Composites Part B: Engineering*, vol. 142, p. 200–220, Jun 2018.
- [10] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, “Detection of individual gas molecules adsorbed on graphene,” *Nature Materials*, vol. 6, no. 9, pp. 652–655, 2007.
- [11] A. Gahoi, S. Wagner, A. Bablich, S. Kataria, V. Passi, and M. C. Lemme, “Contact resistance study of various metal electrodes with cvd graphene,” *Solid-State Electronics*, vol. 125, p. 234–239, Nov 2016.
- [12] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg, and R. S. Ruoff, “Transfer of cvd-grown monolayer graphene onto arbitrary substrates,” *ACS Nano*, vol. 5, p. 6916–6924, Sep 2011.
- [13] K. S. Novoselov, S. V. Morozov, T. M. G. Mohinddin, L. A. Ponomarenko, D. C. Elias, R. Yang, I. I. Barbolina, P. Blake, T. J. Booth, D. Jiang, J. Giesbers, E. W. Hill, and A. K. Geim, “Electronic properties of graphene,” *physica status solidi (b)*, vol. 244, p. 4106–4111, Nov 2007.
- [14] D. J. Finn, M. Lotya, G. Cunningham, R. J. Smith, D. McCloskey, J. F. Donegan, and J. N. Coleman, “Inkjet deposition of liquid-exfoliated graphene and mos2 nanosheets for printed device applications,” *Journal of Materials Chemistry C*, vol. 2, no. 5, p. 925–932, 2014.
- [15] L. Niu, J. N. Coleman, H. Zhang, H. Shin, M. Chhowalla, and Z. Zheng, “Production of two-dimensional nanomaterials via liquid-based direct exfoliation,” *Small*, vol. 12, no. 3, p. 272–293, 2016.

- [16] A. Epstein, “Electrically insulating polymer matrix with conductive path formed in situ 4,841,099,” 1989.
- [17] Robert C. Binning, “Method of graphitizing fibers by laser,” 1972.
- [18] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, and J. M. Tour, “Laser-induced porous graphene films from commercial polymers,” *Nature Communications*, vol. 5, p. 5714, Dec 2014.
- [19] R. W. Dreyfus, “Cn temperatures above laser ablated polyimide,” *Applied Physics A Solids and Surfaces*, vol. 55, p. 335–339, Oct 1992.
- [20] R. Ye, D. K. James, and J. M. Tour, “Laser-induced graphene: From discovery to translation,” *Advanced Materials*, 2018.
- [21] Y. Dong, S. C. Rismiller, and J. Lin, “Molecular dynamic simulation of layered graphene clusters formation from polyimides under extreme conditions,” *Carbon*, vol. 104, p. 47–55, 2016.
- [22] M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio, and R. Saito, “Studying disorder in graphite-based systems by raman spectroscopy,” *Physical Chemistry Chemical Physics*, vol. 9, p. 1276–1291, Mar 2007.
- [23] D. R. Lenski and M. S. Fuhrer, “Raman and optical characterization of multilayer turbostratic graphene grown via chemical vapor deposition,” *Journal of Applied Physics*, vol. 110, no. 1, 2011.
- [24] R. Ye, Y. Chyan, J. Zhang, Y. Li, X. Han, C. Kittrell, and J. M. Tour, “Laser-induced graphene formation on wood,” *Advanced Materials*, vol. 29, no. 37, 2017.
- [25] Y. Chyan, R. Ye, Y. Li, S. P. Singh, C. J. Arnusch, and J. M. Tour, “Laser-induced graphene by multiple lasing: Toward electronics on cloth, paper, and food,” *ACS Nano*, vol. 12, no. 3, p. 2176–2183, 2018.
- [26] R. Ye, D. K. James, and J. M. Tour, “Laser-induced graphene,” *Accounts of Chemical Research*, vol. 51, no. 7, p. 1609–1620, 2018.
- [27] L. X. Duy, Z. Peng, Y. Li, J. Zhang, Y. Ji, and J. M. Tour, “Laser-induced graphene fibers,” *Carbon*, vol. 126, p. 472–479, Jan 2018.
- [28] A. Mannodi-Kanakithodi, G. Pilania, and R. Ramprasad, “Critical assessment of regression-based machine learning methods for polymer dielectrics,” *Computational Materials Science*, vol. 125, p. 123–135, Dec 2016.
- [29] C. Beleites, U. Neugebauer, T. Bocklitz, C. Krafft, and J. Popp, “Sample size planning for classification models,” *Analytica Chimica Acta*, vol. 760, p. 25–33, Jan 2013.
- [30] D. J. Mundfrom, D. G. Shaw, and T. L. Ke, “Minimum sample size recommendations for conducting factor analyses,” *International Journal of Testing*, vol. 5, p. 159–168, Jun 2005.
- [31] J. Hestness, S. Narang, N. Ardalani, G. Diamos, H. Jun, H. Kianinejad, M. M. A. Patwary, Y. Yang, and Y. Zhou, “Deep learning scaling is predictable, empirically,” *arXiv*, Dec 2017.
- [32] M. Burke, A. Blake, I. M. Povey, M. Schmidt, N. Petkov, P. Carolan, and A. J. Quinn, “Low sheet resistance titanium nitride films by low-temperature plasma-enhanced atomic layer deposition using design of experiments methodology,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 32, p. 031506, May 2014.

- [33] S. E. Denmark and C. R. Butler, "Vinylolation of aromatic halides using inexpensive organosilicon reagents. illustration of design of experiment protocols," *Journal of the American Chemical Society*, vol. 130, no. 11, p. 3690–3704, 2008.
- [34] M. J. Anderson, *Know the SCOR for Multifactor Strategy of Experimentation: Screening, Characterization, Optimization and Ruggedness Testing*. 2019.
- [35] C. Felice and D. Qu, "Optimization of the synthesis of nafion-montmorillonite nanocomposite membranes for fuel cell applications through statistical design-of-experiment," *Industrial and Engineering Chemistry Research*, vol. 50, no. 2, p. 721–727, 2011.
- [36] E. Vaughan, C. Larrigy, M. Burke, L. Sygellou, A. J. Quinn, C. Galiotis, and D. Iacopino, "Visible laser scribing fabrication of porous graphitic carbon electrodes: Morphologies, electrochemical properties, and applications as disposable sensor platforms," *ACS Applied Electronic Materials*, vol. 2, p. 3279–3288, Oct 2020.
- [37] A. S. E104-02, "Astm e104," *ASTM International*, vol. 02, no. Reapproved 2012, p. 1–5, 2012.
- [38] A. Tiliakos, C. Ceaus, S. M. Iordache, E. Vasile, and I. Stamatin, "Morphic transitions of nanocarbons via laser pyrolysis of polyimide films," *Journal of Analytical and Applied Pyrolysis*, vol. 121, p. 275–286, 2016.
- [39] R. J. Nemanich and S. A. Solin, "First- and second-order raman scattering from finite-size crystals of graphite," *Physical Review B*, vol. 20, no. 2, p. 392–401, 1979.
- [40] P. Lespade, R. Al-Jishi, and M. S. Dresselhaus, "Model for raman scattering from incompletely graphitized carbons," *Carbon*, vol. 20, no. 5, p. 427–431, 1982.
- [41] A. Eckmann, A. Felten, A. Mishchenko, L. Britnell, R. Krupke, K. S. Novoselov, and C. Casiraghi, "Probing the nature of defects in graphene by raman spectroscopy," *Nano Letters*, vol. 12, no. 8, p. 3925–3930, 2012.
- [42] M. G. Stanford, C. Zhang, J. D. Fowlkes, A. Hoffman, I. N. Ivanov, P. D. Rack, and J. M. Tour, "High-resolution laser-induced graphene. flexible electronics beyond the visible limit," *ACS Applied Materials and Interfaces*, vol. 12, no. 9, p. 10902–10907, 2020.
- [43] M. G. Stanford, K. Yang, Y. Chyan, C. Kittrell, and J. M. Tour, "Laser-induced graphene for flexible and embeddable gas sensors," *ACS Nano*, vol. 13, no. 3, p. 3474–3482, 2019.
- [44] J. Boudaden, M. Steinmaßl, H. E. Endres, A. Drost, I. Eisele, C. Kutter, and P. Müller-Buschbaum, "Polyimide-based capacitive humidity sensor," *Sensors (Switzerland)*, vol. 18, May 2018.

DIRECT-WRITE FORMATION OF INTEGRATED BOTTOM CONTACTS TO LASER-INDUCED GRAPHENE-LIKE CARBON

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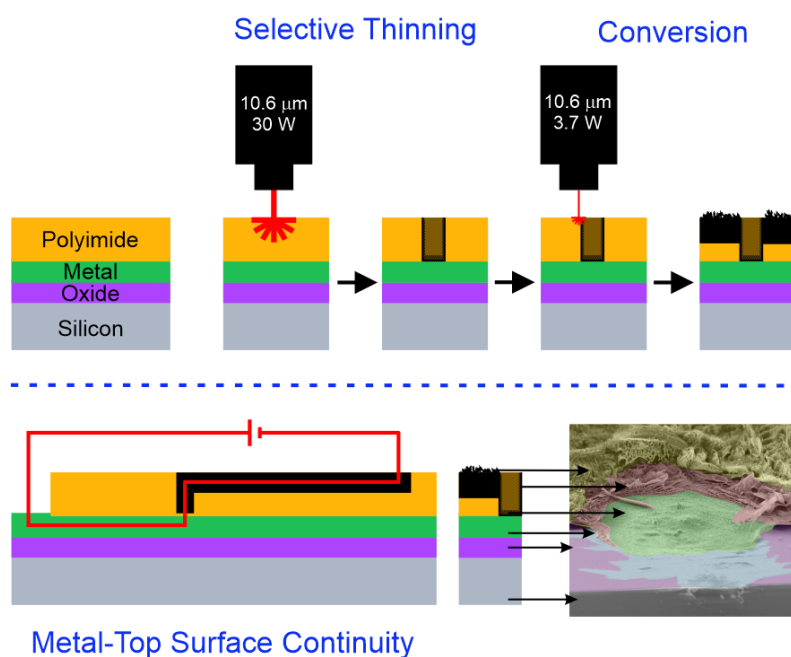


Table of Contents Figure for Direct-write Formation of Integrated Bottom contacts to Laser-Induced Graphene-like Carbon

3.1 Contributions to Knowledge

This paper focuses on the development robust and reliable electric back-contact methods to LIG. Contemporaneous investigations of LIG used silver paint or mechanical contacts which are costly, non-scalable and risk damage/contamination of the active region. No contact methods to LIG had been reported prior to this work. Despite significant investigations into graphene and graphene-like materials, there have been no conclusive determination as to whether physisorbing or chemisorbing metals form better contacts to graphene-like systems. To investigate back-contacting routes to metals of interest it is therefore necessary to use polyimide films of controlled thicknesses on arbitrary metal films, which are not currently commercially available. Further, it is well established that LIG is very sensitive to system conditions requiring processing condition adaptation to account for polyimide thickness, substrate type and laser wavelength, etc..

In this work, I demonstrated the first example of a LIG-metal contact, achieved through a novel all-laser back-contacting method. Following this method I demonstrated the first example of a back contacted LIG based device in application as an electrochemical electrode. This work identified a metal-type dependency on both the magnitude of the contact resistance but also impacted the function of the electrochemical sensor. I also report further routes to decrease the contact resistance through increased scaling of contact number, limiting the application of this method towards sensors over energy storage applications.

This work necessitated the development of a double spin coating fabrication route to prepare sufficiently thick polyimide layers on arbitrary metal films. To reduce experimental resource costs, a non-lithographic route to estimate contact resistance was developed, which allowed for planar metal layers to be used directly.

The control of polyimide thickness afforded by the double spin coating facilitated the demonstration of minimum polyimide thickness required for quality LIG formation $\sim 17 \mu\text{m}$. I further report the bounds of laser conditions attempted that yielded useable contacts, setting the bounds for future optimisation works. The optimal values for contact resistance yield a carbon residue self-encapsulation of the metal layer, preventing it being exposed. Finally, I identified that this contact method, scales with the perimeter of the contact plug, not arealy as is typical with via contacts, which may limit it to sensing applications rather than for energy storage.

Abstract

We report a simple, scalable two-step method for direct-write laser fabrication of 3D, porous graphene-like carbon electrodes from polyimide films with integrated contact plugs to underlying metal layers (Au or Ni). Irradiation at high average CO₂ laser power (30 W) and low scan speed (~ 18 mm/s) leads to formation of “keyhole” contact plugs through local ablation of polyimide (initial thickness $17\ \mu\text{m}$) and graphitization of the plug perimeter wall. Top-surface LIG electrodes are then formed and connected to the plug by raster patterning at lower laser power (3.7 W) and higher scan speed (200 mm/s). Sheet resistance data ($71 \pm 15\ \Omega/\text{sq.}$) indicates formation of high-quality surface LIG, consistent with Raman data which yield sharp first- and second-order peaks. We have also demonstrated that high-quality LIG requires a minimum initial polyimide thickness. Capacitance data measured between surface LIG electrodes and the buried metal film indicate a polyimide layer of thickness $\sim 7\ \mu\text{m}$ remaining following laser processing. By contrast, laser graphitization of polyimide of initial thickness $\sim 8\ \mu\text{m}$ yielded devices with large sheet resistance ($> 1\ \text{k}\Omega/\text{sq.}$). Raman data also indicated significant disorder.

Plug contact resistance values were calculated from analysis of transfer line measurement data for single- and multi-plug test structures. Contacts to buried nickel layers yielded lower plug resistances (1-plug: $158 \pm 7\ \Omega$, 4-plug: $31 \pm 14\ \Omega$) compared to contacts to buried gold (1-plug: $346 \pm 37\ \Omega$, 4-plug: $52 \pm 3\ \Omega$). Further reductions are expected for multi-plug structures with increased areal density.

Proof-of-concept mm-scale LIG electrochemical devices with local contact plugs yielded rapid electron transfer kinetics (rate constant $k_0 \sim 0.017\ \text{cm/s}$), comparable to values measured for exposed Au films ($k_0 \sim 0.023\ \text{cm/s}$). Our results highlight the potential for integration of LIG-based sensor electrodes with semiconductor or roll-to-roll manufacturing.

3.2 Introduction

Laser-induced Graphitic Carbon nanomaterials, often referred to as laser-induced graphene (LIG) materials, have received great interest since the discovery in 2014 of 3D, porous, graphene-like carbon from laser graphitization of polyimide [1]. LIG is attractive due to its high specific surface area, non-lithographic high-precision direct-write patterns and its potential for integration at back-end-of-line in semiconductor processing. These key features have led to applications including gas and electrochemical sensing [2, 3]; energy storage [4, 5]; and integrated heaters [6]. LIG, both as a material and a platform, is rapidly maturing with important progress in theoretical work [7]; optimization of electrical conductivity [8–10]; introduction of alternative synthetic- and bio-based feedstock substrates [4, 11–13]; doping [14–16] and new morphologies [17, 18].

However, one key barrier to successful implementation of LIG-based devices is high contact resistance, a challenge also faced in contacting few-layer graphene devices [19]. Many groups have reported use of silver paint, conductive adhesive or mechanical clips as electrical contacts to LIG devices [17–20]. However, these methods can cause potential contamination due to diffusion of contact materials and/or mechanical damage to the LIG device, thus posing integration challenges for high-volume device fabrication. More recently, cured silver nanoparticle inks, using polyimide-self masking, have been demonstrated to reduce the sheet resistance [21, 22]. Similarly, electroless plating of the LIG top surface has also been demonstrated to produce metal coated LIG electrochemical working electrodes [23]. While these methods show promise, their use of costly inks/plating agents and modification of the pristine LIG material platform could be avoided through previously unconsidered bottom contact geometries, simplifying process steps without additional post processing.

The optimizations presented in this work are essential as device resistance is more complex than traditional resistivity ($R = \rho L/A$), containing multiple contributions. It is useful to instead consider length-dependent and length-independent factors. The standard test structure to characterize these is a TLM device, where resistance between a series of locations at known separations and fixed width are measured. The dataset is plotted as $R_T(L) = R_{Ch} \times L + R_C$, where R_T is the total resistance, R_{Ch} is the length dependent channel resistance, and R_C is the contact resistance. The channel contribution is analogous to the traditional resistivity view, while

the contact resistance accounts for additional parasitic components such as barriers to charge injection or iR drop-off. This contribution is detrimental to practical devices and should be minimized.

Graphene and graphene-like materials are not sufficiently mechanically or chemically robust enough to employ traditional processes (doping, annealing etc.) used in conventional semiconductor fabrication to mitigate charge injection barriers and achieve band-alignment [24]. Optimizing contacts to planar graphene devices remains the subject of intense, ongoing research and a brief summary is provided in the supplementary information, SI-3.1. LIG can be considered graphene-like on small length scales, with high relatively densities of edge defects [1]. The key issues are the choice of contact metal, impact of interfacial residue and contact geometry.

Metal-graphene contacts can be broadly divided into two classes: Chemisorbing (bonding) metals such as nickel, and physisorbing (charge transfer) metals such as gold. Chemisorbing metals normally form bonds to graphene at defect- or edge-sites due to their higher energy density. These bonds can reduce injection barriers, thereby reducing the contact resistance, but can also lead to charge redistribution and deviation from electronic properties of pristine graphene. Physisorbed metals not only experience injection barriers but also are impacted by unintentional doping which can lead to local p/n junction formation and increases in contact resistance.

Interfacial residues in pristine graphene often originate from polymer handling layers or photoresist and can act as adsorbate dopants (or tunnel barriers), compromising efficient charge injection. Unfortunately, traditional cleaning methods can often lead to unwanted graphene damage. Methods like shadow deposition, edge or bottom contacts have been demonstrated for monolayer graphene systems to mitigate their influence [25–27]. While LIG processes don't involve handling layers, interfacial residue can arise from unconverted or laser-displaced polyimide or other polymer residue (e.g., from adhesion promoters). Edge-contacts, have been developed to address these challenges for graphene systems. Edge-contacting involves accessing each graphene sheet through dangling bonds at the perimeter. The number of edge sites can be increased through controlled etches, lithography and laser treatments. Chemisorbed metals experience a greater reduction in contact resistance when edge contacting, largely due to

carbide formation. LIG is a graphene-like material with numerous edge sites, already primed for edge-contacting approaches.

Here we report a simple, scalable method for direct-write laser fabrication of low-resistance contacts to LIG structures. Starting from spun-cast polyimide films on top of buried metal layers - Au or Ni - we have developed a simple, self-aligning two-step laser process to define contact plugs at $\sim 200\ \mu\text{m}$ length scales. The first step employs $\sim 30\ \text{W}$ average laser power to locally ablate polyimide, creating a via with a partially graphitized contact plug perimeter. The second step uses a lower average power ($\sim 3.7\ \text{W}$) to raster-pattern a conventional LIG electrode around the contact plug. This approach minimizes resistive (iR) potential drops and enables full use of the LIG surface area, while minimizing contamination. The addition of the first laser step to selectively pre-thin the film negligibly increases processing time, due to the small feature dimensions (single laser pulses). The second write can then be carried out immediately ensuring good alignment, requiring equivalent processing time to non-back contacted devices while removing the need to separately contact the structure, as is currently the case for Ag paint/mechanical methods.

We demonstrate that the contact resistance scales with the perimeter of the contacting structure and can be reduced by increasing the areal density of the contact plugs. We have also investigated proof-of-concept electrochemical devices. The influence of channel resistance on sensing is highlighted as well as proof-of-concept demonstrations of electrochemical functionality for contact plugs exposed to electrolytes containing redox molecules. Our results highlight the potential for efficient integration of LIG-based, high-surface area electrodes with buried metal layers.

3.3 Experimental Methods

3.3.1 Polyimide-metal Stack Preparation

Metal Layers

100 mm diameter Si wafers were cleaned (Semitool SAT tool, hot deionized water, ozone, NH_4OH , dilute HF) prior to oxidization. ~ 300 nm of SiO_2 was formed by wet thermal oxidation (1100°C , 16 min, atmospheric pressure, Thermoco 9000 series). For Ni-terminated wafers, 100 nm of Ni was thermally evaporated directly onto the SiO_2 layer. For Au-terminated wafers, 10 nm of Ti was first deposited to promote adhesion, followed by 100 nm of Au.

Polyimide Layer

A double layer of polyimide precursor (PI5878G) was spin-coated on the metallized wafers. This was achieved by first depositing an adhesion promoter (VM652) and spinning to ensure a conformal layer (5 s @ 500 rpm, 10 s @ 1000 rpm, 30 s @ 2000 rpm). Subsequently the polyimide precursor was deposited and spun (5s @ 500 rpm, 10 s @ 1000 rpm, 30 s @ 2000 rpm) and soft baked (1 min, 120°C), allowed to cool (1 min) and further soft baked (4 min, 140°C). A second spin coating of the polyimide precursor was then carried out, following the same methodology, but without the adhesion promoter. The polyimide precursor stack was then hard-baked (ramp-up to 200°C @ $4^\circ\text{C}/\text{min}$, hold at 200°C for 30 min, ramp up from 200°C to 300°C @ $4^\circ\text{C}/\text{min}$, hold at 300°C for 60 minutes, ramp-down at $5^\circ\text{C}/\text{min}$ and cooled overnight).

Laser Graphitisation

Polyimide-coated wafers were scribed and cleaved by hand. Contact plugs were produced using a $10.6\ \mu\text{m}$ CO_2 laser (Universal Laser System 4.75, 30 W max. average power). A double-pixel contact plug pattern was written at 30 W average power and ~ 18 mm/s scan speed. The top-surface LIG structure was then superimposed on the contact plug by raster patterning at 3.7 W average laser power, ~ 200 mm/s scan speed (500 PPI) and ~ 20 lines/mm raster line density.

3.3.2 Microscopy

Sample Cross Sectioning

To avoid mechanical damage to the brittle laser-induced graphene surfaces of interest careful mechanical cleavage steps were used. The supporting wafer was cleaved using a diamond scribe, so that the crystalline plane aligned with the previously patterned contact plug. The polyimide and metal layers were then cut using a sharp scalpel adjacent to the region of interest, taking care not to damage the LIG. The remaining connecting material comprised a thin layer of polyimide, metal layer and LIG, were separated by pulling the two wafer sections apart perpendicular to the cleavage direction, ensuring that the wall material doesn't become damaged through compression.

Microscopy Methods

White light and epifluorescence micrographs were acquired using a Zeiss Axioscope 2 (546 $\pm$ 12 nm bandpass excitation filter, >590 nm longpass emission filter). Scanning electron microscopy (SEM) images were recorded using a Carl Zeiss Supra Scanning electron microscope (10 keV) with connected Oxford Instruments X-Max 50 for EDX. EDX was recorded under the same conditions as the SEM (10 keV).

3.3.3 Raman Spectroscopy

Multiple locations within the contact plug and at the top surface LIG were analyzed using Raman spectroscopy. Due to the interest in the wall of the contact plug, two different sampling geometries were necessary. Top surface and plug base measurements were achieved by measuring as-fabricated samples. Cross-sectioning and sample tilting was necessary to probe the plug sidewall. Raman sampling was performed (Renishaw inVia, 514.5 nm Ar laser, 50 $\times$ objectives) with five accumulations. Multiple locations were sampled in each configuration to ensure representative spectra for each region of interest.

3.3.4 Electrical Characterisation

Electrical characterization was achieved by landing probes onto either exposed base metal or on top of LIG test structures with channel widths of 3 mm and lengths up to 25 mm. Devices with one probe contacting the surface LIG and one probe contacting an exposed region of the buried metal layer are referred to as bottom contacts. Devices where both probes contacting surface LIG structure are referred to as top contacts. These contacts were made at known channel lengths, designated by guide structures, produced during laser conversion. Potential-current (I-V) sweeps were acquired (Wentworth PML 8000 probe station, Agilent E4980A parameter analyzer, ± 100 mV sweeps, 10 mV step) at each location. Device resistance values for each value of channel length were extracted from linear fits to corresponding I-V data. Transfer line measurement (TLM) plots of resistance vs channel length were used to calculate the sheet resistance for each device (from the slope of a linear fit) and contact resistances (from the intercept).

3.4 Results and Discussion

Figure 3.1a-c shows a schematic of the laser-defined contact plug process. The polyimide film ($\sim 17 \mu\text{m}$ thick) was formed by two sequential spin-coating/curing steps onto a metallized wafer substrate (schematic in Fig. 3.1a). Gold or nickel layers were deposited on thermally oxidized silicon substrates, i.e. Si/SiO₂/Ti (10 nm)/Au (100 nm) or Si/SiO₂/Ni (100 nm). The first laser processing step (Lase#1) at maximum average power (100% = 30 W) and minimum scan speed (~ 18 mm/s) of a double-pixel linear pattern led to formation of a contact plug structure (Fig. 3.1b). Fig. 3.1d shows a white-light micrograph of an array of single-lased double-pixel “keyhole” structures and Fig. 3.1e shows a higher magnification micrograph of a single keyhole. The data are consistent with ablation of polyimide at the center of each pixel (laser focus), together with laser-induced graphitization around the perimeter due to lower local laser fluence, as expected for a Gaussian beam profile. Initial single step plug structures were attempted at various average laser powers (30, 17.5, 15 W). Continuity between the base metal and annulus of top surface material was achieved. The lowest resistance was observed for the 30 W write (200 Ω vs. 500 Ω for the 15 W write). To produce higher surface area material with a known

contacting geometry, the second laser step (Lase#2) comprising raster-patterning at low average power (~ 3.7 W) and higher scan speed (~ 200 mm/s) was employed, forming surface LIG in a rectangular region around the keyhole plug (Fig. 3.1c, optical micrographs in Fig. 3.1f,g).

As will be demonstrated in this work, this combination of parameters (Lase#1 30 W, 18 mm/s, Lase#2 3.7 W, 200 mm/s) results in good quality top surface LIG electrically connected to the buried metal layer. This is a rich opportunity for multifactor optimization due to the complex inter-relationship of different laser-conditions. Considering also the polymer thickness and formulation, Design of Experiment methods would be a future resource efficient optimization for this system [8]. With this pathway in mind, this simple method offers significant opportunities for direct-write formation of LIG structures with an integrated electrical contact to a buried metal layer. The supporting wafer acts as a mechanical support and allowed for the tuning of polyimide thickness and physi-/chemi-sorbing contacting metal. However, the wafer support is not essential and this process could also be extended to commercially available, flexible, polyimide-on-metal films to produce bottom contacts to LIG.

Epifluorescence data (546 ± 12 nm bandpass excitation, >590 nm longpass emission filter) of double-written patterns reveal uniform strong fluorescence from the un-lased polyimide regions (Fig. 3.1h), strong fluorescence at some perimeter regions of the keyhole structure (Fig. 3.1i) and weak fluorescence from the regions of the keyhole structure that show iridescence under white light illumination (Fig. 3.1g). Taken together, these data suggest the presence of a residue layer on top of the buried metal film.

SEM data support this hypothesis. Fig. 3.2a shows SEM images of keyhole contact plugs, the lower feature surrounded by polyimide, formed by lase#1, shows removal of significant quantities of polyimide by the high-power ablation step (Lase#1), together with evidence of laser-graphitized carbon in the semi-porous perimeter around the ablated keyhole. This semi-porous morphology has been previously observed in partially-graphitized polyimide using a 500 mW 405 nm laser [3]. Different morphologies of LIG are seen in region of the contact plugs, regardless of the underlying metal: Highly porous LIG structures in top surface regions only exposed to the Lase#2 step, seen in the top region of Fig. 3.2a; layered structures at the sidewall perimeter of the keyhole structure; and a more continuous layer at the base of each keyhole as

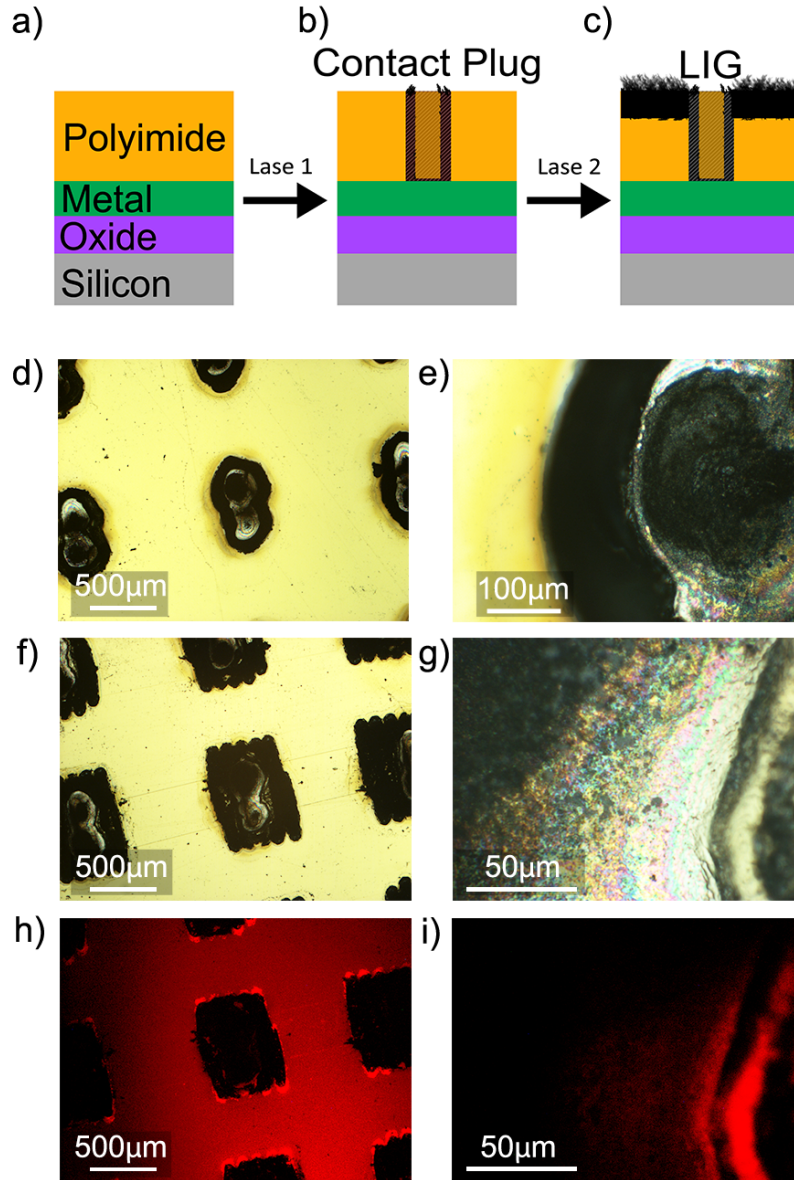


Figure 3.1: Schematic cross sections of (a) polyimide layer deposited on metal film on oxidized silicon substrate; (b) Contact plug formed by first laser step - high power, low scan speed two-pixel linear pattern leading to material ablation and partial graphitization forming a quasi-tubular contact plug structure; (c) Surface LIG pattern formed by second laser step (lower-power rastering). Low-magnification (d) and high magnification (e) white-light micrographs acquired after the first laser step. (f, g) Corresponding micrographs acquired after the second laser step (h, i) Epifluorescence micrographs from the same regions acquired (546 ± 12 nm bandpass excitation, >590 nm longpass emission).

shown in Fig. 3.2b,c. (equivalent micrographs for Au-terminated devices are presented in Fig. SI-3.1). Further investigation of the transition region between the wall and the base, Fig. SI-3.2, highlight the layered, flake-like structure connecting the base and the wall. Interestingly, the contrast in the top-view SEMs, Fig 3.2c, suggest significant damage to the buried Ni layer at both

laser foci for the double-pixel keyhole structure, which is not observed for the Au-terminated devices.

EDX maps for Ni-terminated devices show a reduction in the Ni signal and an enhancement of the Si signal at both foci (Fig. 3.2e,f), consistent with local ablation of Ni. By contrast, a uniform Au signal is evident in the EDX map within the keyhole region for the buried Au layer (Fig. SI-3.1e) suggesting less damage to the underlying metal layer for Au-terminated wafers. Unlike Au, Ni forms metal carbides and oxides easily. It is for this reason that Ni has been of great interest in the graphene literature as a chemisorbing metal. During the lasing process a high-energy-plasma forms *in situ* which allows for restructuring of graphene-like material. This excitation would facilitate the formation of Ni–C and Ni–O bonds, damaging the, initially planar, Ni surface; exposing the Si, as seen in the EDX map, Fig. 3.2f. These new groups and bonds could also limit the ability of the metal to survive further irradiation.

Raman spectroscopy was employed to gain further insight into the carbon phases of the different regions: contact plug base, plug side wall and the top surface LIG, distant from the plug. Fig. 3.3a shows a false-color representation of the SEM data to highlight the different regions. Fig. 3.3b-d show representative Raman spectra from the top surface, base, and sidewall regions, respectively. Table 3.1 summarizes the results extracted from Lorentzian fits to the first order peaks (D, D', G) and the second-order 2D peak [8, 28, 29]. The top-surface LIG Raman spectrum shows sharp first- and second-order peaks, with FWHM values (D: $< 50\text{ cm}^{-1}$, G: $< 40\text{ cm}^{-1}$, 2D: $< 70\text{ cm}^{-1}$) comparable to those measured for LIG fabricated from thicker polyimide tape samples using the same laser system [8]. Fits to Raman data from the sidewall region yield slightly broader peaks with a more intense D peak, indicating increased disorder in the sidewall region (both laser steps) vs. the top surface region (Lase#2 only). The Raman data measured in the base region reveal significantly broader D, G, 2D peaks, consistent with nanocrystalline graphitic regions in an amorphous carbon matrix [3, 30].

Raman data acquired in the base region following the first laser step show evidence of high-quality LIG formation for Au-terminated samples (Fig SI-3.4c), with more defective LIG formed at the base of Ni-terminated samples (Fig. SI-3.4a). This corresponds with our previous suggestion of Ni-Carbide and Ni-Oxide groups forming due to its higher reactivity, limiting the

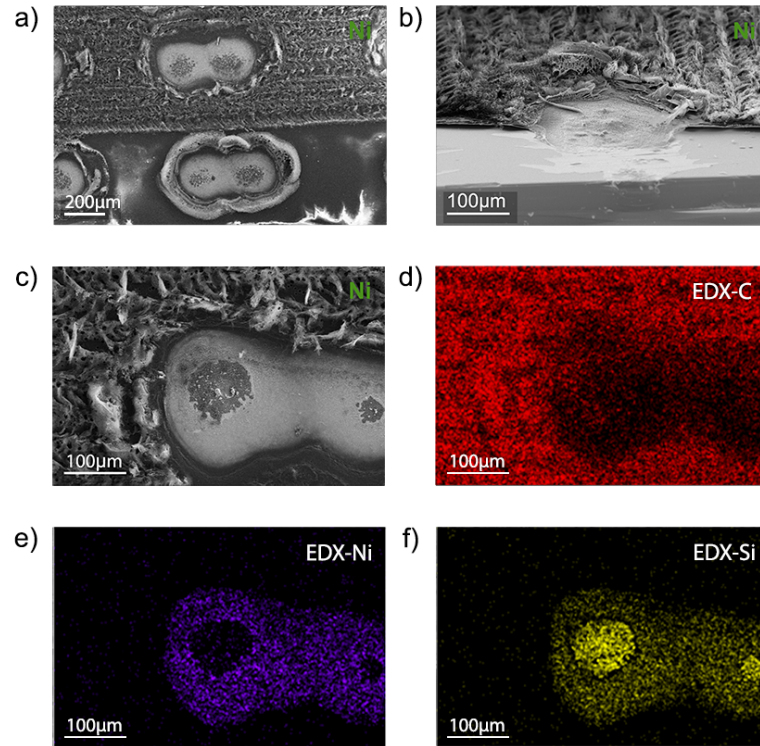


Figure 3.2: Scanning electron microscopy (SEM) data: a) Planar SEM of keyhole contact plugs formed by local laser ablation of polyimide deposited on a Ni-terminated Si/SiO₂ wafer. The upper section shows a double-written region with surface LIG surrounding the contact plugs. b) Cross-sectional SEM of mechanically cleaved LIG contact plug on Ni-terminated wafer after the second laser write. c) Higher magnification view of a contact plug following the second laser step on a Ni-terminated wafer. d-f) EDX maps of a contact plug following the second laser step on a Ni-terminated wafer demonstrating spatially defined abundance of d): Carbon, e): Nickel and f): Silicon.

graphene-like quality of the base material. Following the second write step the Raman quality of both the Ni and Au terminated samples become equivalent (Fig SI-3.4b,d), demonstrating damage from the second laser write. Taken together, the optical, SEM and Raman data highlight the utility of this simple two-step laser contacting method. Although some variability was observed in terms of keyhole dimensions and laser-induced changes to the underlying metal layer for Ni samples, these issues could be mitigated in future by employing single pixel structures or vector mode patterning for the first laser step, together with multiple laser pulses at lower average power per pixel [9, 12]. The site- and process-dependent morphology may also present opportunities for future device development.

Simple two-terminal test structures were devised to facilitate rapid optimization of the metal-LIG contact plug with minimal processing. Figure 3.4 shows a cross-sectional schematic of a

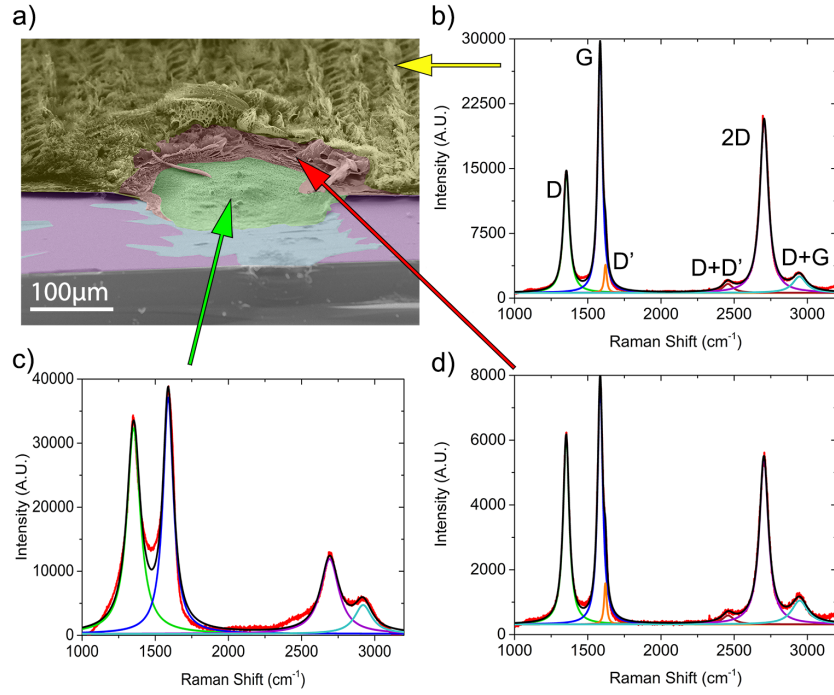


Figure 3.3: a) False color SEM micrograph: purple - silicon oxide, blue - exposed Ni, green - contact plug base, red - contact plug sidewall, yellow - top surface LIG. b-d) Representative Raman spectra from top surface, base of contact plug and plug sidewall, respectively.

Table 3.1: Compiled Raman fit characteristics for top surface, plug base and plug sidewall graphitic material formed on Ni-terminated wafer fit using Lorentzian peaks. No D' peak could be extracted for the spectra from the plug base. A/A_G refers to the peak area as a fraction of the area under the G peak.

	Top Surface			Plug Base			Plug Sidewall		
	Peak Pos (cm^{-1})	FWHM (cm^{-1})	A/A_G	Peak Pos (cm^{-1})	FWHM (cm^{-1})	A/A_G	Peak Pos (cm^{-1})	FWHM (cm^{-1})	A/A_G
D	1354	50	0.65	1352	110	1.11	1353	50	0.94
G	1584	37	n/a	1589	86	n/a	1585	42	n/a
D'	1621	21	0.06	Absent			1621	21	0.09
2D	2704	69	1.30	2692	150	0.55	2703	75	1.23

“top-contacted” test structure, where the current flows through the surface LIG region between two rounded probe needles, each with $\sim 0.25 \text{ mm}^2$ contact area. Figure 3.4b shows a schematic of a “bottom-contacted” test structure with one probe contacting the top LIG surface and the second probe contacting an exposed region of the metal layer, such that the current flows through the laser-defined contact plug. Two test structure geometries were developed for each contact type: simple bar structures with a single contact plug to the underlying metal (Fig. 3.4c, inset) and “lollipop” structures with four parallel contact plugs (Fig. 3.4d inset). For each geometry,

the current-voltage (I-V) characteristics were measured as a function of the channel length, L . For each top-contacted bar structure, one probe was maintained at a fixed location ($L = 0$) and I-V characteristics were acquired with the second probe located at $L=25, 20, 15, 10, 5$ mm, respectively (Fig. 3.4c). For each top-contacted lollipop structure, the fixed probe contacted the center of the lollipop head (Fig. SI-3.5) and the second probe was moved from $L = 25$ mm to $L = 0$ mm in 5 mm steps (Fig. 3.4d). For bottom-contacted bar and lollipop structures, the fixed location probe contacted an exposed region of the buried metal layer (Fig. 3.4b). This resource-efficient method allows us to gain insight into the contributions of the contact plug to the total device resistance.

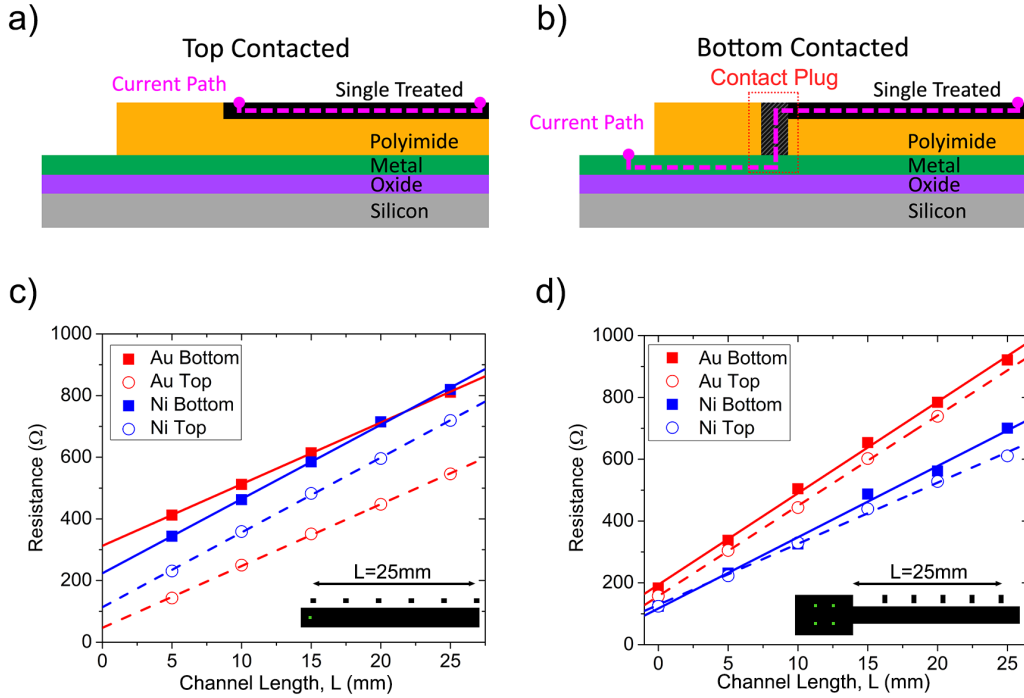


Figure 3.4: Schematic cross-sections showing current paths for: (a) top-contacted structures with both probe needles (pink circles) landing on surface LIG; (b) bottom-contacted structures with one probe on an exposed section of buried metal (Au or Ni). (c) Transfer Line Measurement (TLM) data of resistance vs channel length (L) and linear fits for “bar” test structures with single contact plugs (green square in inset schematic) in bottom- and top-contacting geometries for both Au- and Ni-terminated devices (channel widths: 3 mm). (d) TLM data and fits for “lollipop” test structures (4 parallel contact plugs).

Figure 3.4c,d show representative resistance vs channel length measurements for individual top- and bottom-contacted bar and lollipop structures, respectively, for both Au- and Ni-terminated devices. The sheet resistance for each device is calculated as, $R_{sh} = slope \times W$,

where all devices had the same channel width ($W = 3$ mm). We note that individual pairs of devices had similar sheet resistances, as expected.

Table 3.2: Averaged sheet resistance and intercept resistance (with standard error on mean) from multiple transfer line measurements across different geometries. The labels follow the following convention $R_{Contact\ Geometry}^{Lollipop(L)/Bar-Metal(Au/Ni)}$.

<i>Bar</i>	n	Sheet Res.	Intercept	<i>Lollipop</i>	n	Sheet Res.	Intercept
R_{Top}^{Bar-Au}	4	58 ± 1	44 ± 6	R_{Top}^{L-Au}	3	78 ± 3	180 ± 10
R_{Bot}^{Bar-Au}	4	60 ± 1	368 ± 40	R_{Bot}^{L-Au}	3	96 ± 6	210 ± 9
R_{Top}^{Bar-Ni}	4	78 ± 2	113 ± 19	R_{Top}^{L-Ni}	2	58 ± 2	125 ± 3
R_{Bot}^{Bar-Ni}	2	82 ± 7	215 ± 6	R_{Bot}^{L-Ni}	2	60 ± 6	101 ± 11

Table 3.2 shows extracted values of the sheet resistance and intercept resistance, averaged over multiple devices (n) for each geometry and metal, mitigating device-to-device variability of contact geometry and process conditions. The LIG sheet resistance values are quite consistent across the 24 devices ($R_{sh,mean} = 71$ $\Omega/\text{sq.}$, standard deviation 15 $\Omega/\text{sq.}$), even for such a small thickness of polyimide (~ 17 μm). Iterative optimization methods could be used to lower the sheet resistance further. Values of ~ 16 $\Omega/\text{sq.}$ have been reported for thicker (~ 70 μm), drawn polyimide films [8], although thicker films may lead to lower sheet resistance due to enhanced thermal decoupling from the substrate [7].

Raman spectra from LIG fabricated from thinner polyimide films (~ 8.5 μm) deposited on Si/SiO₂ substrates indicated significant disorder (Fig. SI-3.9a). Measured sheet resistances exceeded 1 k $\Omega/\text{sq.}$, vs. ~ 75 $\Omega/\text{sq.}$ values measured for LIG fabricated from 17 μm polyimide films on the same Si/SiO₂ substrates. This suggests that a minimum thickness of polyimide may be necessary in order to generate high-quality LIG, possibly due to the need to create a thermal barrier in order to maintain the local high temperature required for graphitization [7]. Capacitance measurements on LIG test structures fabricated from 17 μm polyimide on Au-terminated Si/SiO₂ substrates showed the expected areal scaling (Figure SI-3.10b), allowing the thickness of unconverted polyimide to be estimated (~ 7 μm). This residual polyimide layer showed no evidence of breakdown up to 20 V, thus functioning as a high-quality dielectric. While this residual polyimide may offer opportunities for some applications, it highlights the necessity to form low-resistance contact plugs to the underlying metal. This implies that during its formation, the top-surface LIG material is independent of the base metal. Therefore, the sheet

resistances of the top-surface material quality should be equivalent within experimental variation, if the polyimide thickness provides sufficient insulation.

The resistance of the contact plugs for the different geometries and contact metals can be estimated from the intercepts to the TLM plots for bottom-contacted devices. It is immediately evident from Fig. 3.4c&d that moving from a single plug to four plugs results in a significant reduction in contact resistance for both Ni- and Au-based devices. Data from top-contacted structures can be used to estimate the probe-LIG interface resistance (see Section SI-3.4) and thus calculate the resistance of the contact plug structure(s); see Table 3.3. The results suggest lower contact resistance for Ni-based plugs, as expected for a chemisorbing metal. The four-plug structures show resistances $\sim 52 \text{ } \Omega$ for Au and $\sim 31 \text{ } \Omega$ for Ni. Given the footprint area of the plugs ($\sim 450 \text{ } \mu\text{m} \times 225 \text{ } \mu\text{m}$) and the plug pitch for the 4-plug array ($\sim 3 \text{ mm}$), it should be possible to achieve a further ~ 5 -fold reduction in resistance for the contact structure, simply by increasing the areal density of contact plugs to a 6×4 array, even with a conservative inter-plug spacing of $250 \text{ } \mu\text{m}$.

Table 3.3: Estimated plug resistance values for single- and four-plug devices extracted from TLM data for bar and lollipop test structures (see supplementary information, SI-3.4). Errors provided are based on the extrema of standard errors of the underlying dataset used in their estimation.

Au:1-Plug	Au: 4-Plug	Ni: 1-Plug	Ni:4-Plug
$346 \pm 37 \text{ } \Omega$	$52 \pm 3 \text{ } \Omega$	$158 \pm 7 \text{ } \Omega$	$31 \pm 14 \text{ } \Omega$

The contacting structure between the base metal and the top-surface material comprises of three parts: the metal interface, transfer along the base and transfer up the plug wall. Scaling the contact plug size results in a perimeter scaling of the contact resistance instead of the typical areal scaling of the contact (see section SI-3.5), with estimated resistivity of $0.3 \text{ } \Omega\text{m}$, significantly larger than the c-axis resistivity for bulk graphite ($3 \times 10^{-3} \text{ } \Omega\text{m}$) [31]. Without significant optimization work to decrease this resistivity, lateral transfer across the base would be a minimal contribution, resulting in the conduction through the perimeter of the contact near the wall region. Therefore, the plug resistance can be considered as two components in series: the metal-LIG interface and the “wall” to the top surface LIG. These components cannot be easily separated for consideration as, the base metal controls both the allowed process (physi-/chemi-sorption)

but also the extent of damage/conversion done to the wall region in the first laser write process. The quality of the wall material above a given metal surface at any particular laser condition is an intrinsic property of that system for the purposes of application and optimization. The base contact contribution could be improved through increasing the areal density of the keyhole plugs and optimizing the perimeter-footprint ratios.

Similarly, lithographic processing could also be used to locally thin the polyimide film (minimizing the current path contact plug, while allowing for gentler, more optimal laser formation conditions), however scalable methods compatible with roll-to-roll processing would be preferable, e.g., shadow masking, imprint approaches and/or plasma treatment to thin the precursor polyimide locally. Developing these approaches to maximize the available LIG surface area while minimizing the overall contact resistance will be a key future challenge.

Electrochemistry illustrates the importance of reducing parasitic components (e.g. contact and sheet resistance). We present results from a number of LIG working electrode geometries for cyclic voltammetry of a well established model redox probe, 5mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 1M KCl supporting electrolyte to demonstrate critical necessity of reducing the access resistance for any LIG-based electrochemical system. Electrochemical sensors often suffer from fouling, thus inexpensive, disposable replacement would be of great interest [3, 32, 33].

Fig. 3.5a compares the electrochemical response (0.1 - 0.45 V, 100 mV/s) for 3 mm wide LIG working electrodes using three different contacting methods: a spring-loaded metal clip which mechanically contacts the top-surface LIG outside the electrochemical working electrode region defined by the o-ring; and bottom-contacted LIG structures with the contact plug arrays to the buried Au layer inside the sensing region (internal) or outside (external), respectively. An equivalent area of the exposed Au layer was also characterized for comparison. Peak separation (ΔE_p) values of 136 mV, 96 mV, 165 mV, 69 mV were found for the external clip, internal plug, external plug and exposed Au electrochemical devices respectively. As expected, the external mechanical clip and external plugs show the largest ΔE_p values due to access resistance. The value for the internal contact plug array (96 mV), is much closer to the value for exposed planar Au (69 mV), which approaches an ideal Nernstian response ($\Delta E_p = 57$ mV at 25°C) [33].

A lollipop test structure with 4 external contact plugs (Fig. 3.5b, upper inset) was used to

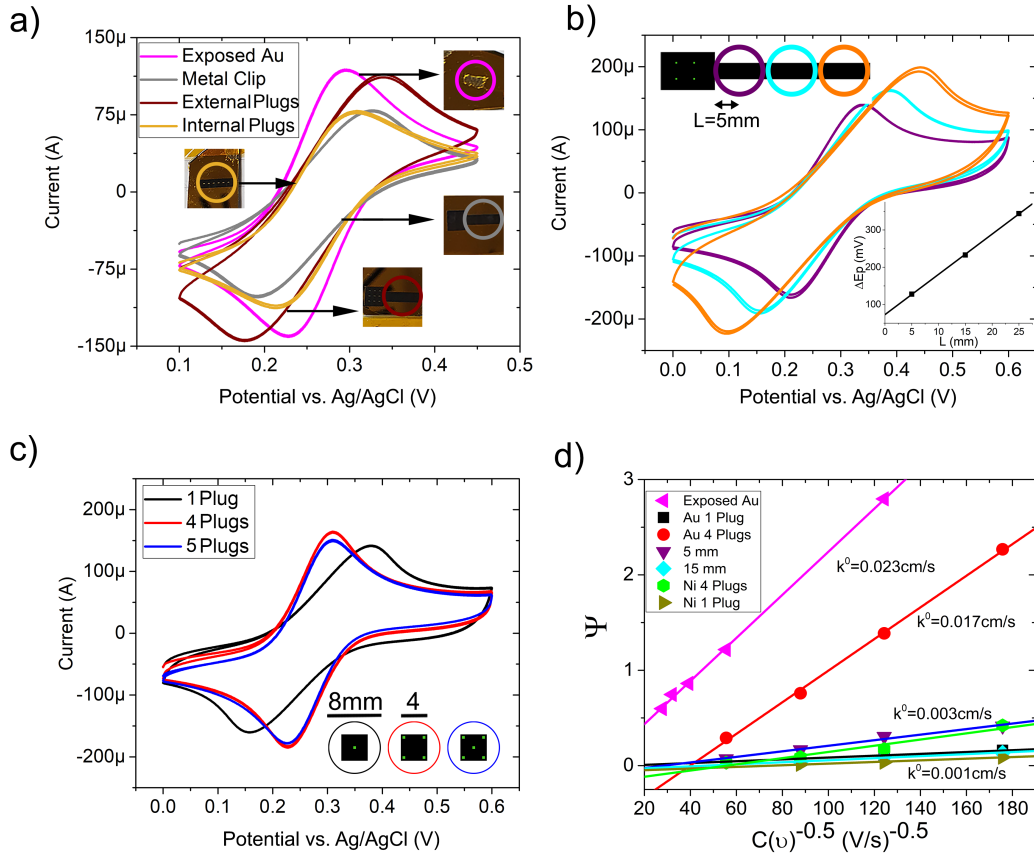


Figure 3.5: (a) CV scans (100 mV/s) for 5 mM ferrocyanide for LIG working electrodes with different access contact geometries: External metal clip to surface LIG; 6×1 internal contact plugs to buried Au layer; 3×3 internal contact plugs; Exposed. Inset are images of the electrochemically active region marked circle demonstrating the 8mm diameter o-ring used. (b) CV scans for different access channel lengths, $L = 5, 10, 15$ mm. Upper inset: Device schematic. Lower inset: Peak separation (ΔE_p) vs. channel length, L . (c) CV scans for different internal plug structures (1, 4, 5 plugs) each overlaid with a 4×4 mm² LIG electrode. Inset: Device schematics. (d) Comparison of electrochemical kinetics for different contacting structures.

investigate the influence of access resistance by measuring cyclic voltammograms (0 - 0.6 V, 100 mV/s) as a function of the channel length (L) for $L = 25, 15, 5$ mm. The voltammograms for longer-channel devices show significant distortion and increased ΔE_p values. A linear fit to the ΔE_p vs. L data (Fig. 3.5b, lower inset) yields a projected $\Delta E_p = 73$ mV at zero channel length, illustrating that external contact plugs fabricated close to the working electrode region can significantly improve device performance. The influence of internal contact plugs was also studied (Fig. 3.5c). For these experiments, test structures were fabricated with different numbers of contact plugs (1, 4, 5) using the first laser step. A 4×4 mm² top-surface LIG pattern was overlaid using the second step in order to avoid mechanical contact with the O-ring of the

electrochemical cell. It is evident from the large peak separation ($\Delta E_p = 223$ mV) and reduced peak current that a single plug is not sufficient to approach Nernstian behavior. However the 4- and 5-plug structures to the buried Au layer both show $\Delta E_p = 84$ mV, indicating an efficient contact, in line with previous work on LIG electrodes externally contacted with silver paint [32]. By contrast, test structures with contact plugs to buried Ni layers (Figure SI-3.14) showed increased peak separations, $\Delta E_p = 340$ mV, 183 mV and 167 mV for 1-, 4- and 5- plug structures.

Fig. 3.5d shows the Nicholson kinetic parameter, Ψ (Equ. 3.1), plotted for each test structure vs. $C\nu^{-0.5}$ where ν is the scan rate (see Equ. 3.2 for definition of C) [33, 34]. The ΔE_p values in this work can exceed the limits of the Nicholson kinetic parameter equation, in these cases it is necessary to use the Klingler and Kochi estimation for Ψ (Equ. 3.3) at large ΔE_p (>150 mV) [35–37]. The heterogeneous electron transfer rate, k_0 , was calculated for each structure from the slope. The LIG structure with a 4-plug internal contact to buried Au showed the best electron transfer rate, $k_0 \sim 0.017$ cm/s, comparable with reported values for LIG devices optimized for electrochemistry, 0.013 - 0.126 cm/s [3, 32]. The lower values for single-plug contacts, external plug contacts and plugs to buried Ni layers highlight the importance of access channel resistance and contact resistance for electrochemical sensor devices, particularly where high scan rates are needed. Our simple, scalable laser process could be further optimized to produce arrays of diffusionally-independent LIG electrodes, each with a low-resistance plug to a buried metal current collector, without the need for expensive and resource-intensive lithography.

$$\psi = \frac{(-0.6288 + 0.0021n\Delta E_p)}{1 - 0.017n\Delta E_p} \quad (3.1)$$

$$C = (D_0/D_r)^{\frac{\alpha}{2}} \frac{1}{\sqrt{\pi D_0 n F / RT}} \quad (3.2)$$

$$\Psi = 2.18 \sqrt{\frac{\beta}{\pi}} \exp(-(\beta^2 F / RT)n\Delta E_p) \quad (3.3)$$

n : number of electrons transferred; ΔE_p : separation between the anodic and cathodic peaks; $D_{o/r}$: diffusion coefficient of the oxidized/reduced species; α Charge transfer coefficient; β transfer coefficient for the electrode process. Other symbols have their usual meaning.

3.5 Conclusions

Our simple direct-write laser method enables rapid fabrication of LIG structures with integrated low-resistance contact plugs to buried metal layers. The contact resistance can be reduced to $\sim 30 \Omega$ for Ni layers ($\sim 50 \Omega$ for Au) using 4-plugs in parallel. We expect a further 5-fold reduction in contact resistance by increasing the areal density of the plugs. We have also demonstrated that a minimum layer thickness of polyimide is needed for production of high-quality LIG: Raman data for laser graphitized polyimide films with starting thickness $\sim 8 \mu\text{m}$ show significant disorder, whereas lasing $\sim 17 \mu\text{m}$ films produces high-quality surface LIG which consumes $\sim 10 \mu\text{m}$ of the starting material. Our proof-of-concept electrochemical devices show the value of internal contact plugs as a mean to achieve rapid kinetics. These results highlight the potential for efficient integration of LIG-based, high-surface area sensor electrodes with buried metal layers. Although Ni layers produced lower contact resistances, Au layers produced devices with lower variability in electrochemical applications, suggesting application specific optimization of contact structures should be considered. Finally, we note that the silicon wafer substrates used in this work are not an essential component for the process and that flexible polyimide-on-metal films are commercially available. Therefore, this simple, scalable, non-lithographic, direct-write laser processes should be compatible with roll-to-roll electronics manufacturing as well as back-end-of-line semiconductor manufacturing for future production of LIG-based sensors.

SI-3.1 Graphene Contact Resistance Literature Review

Contact resistance challenges are a key barrier to development of graphene-based electronic devices [38]. LIG similarly requires low contact resistance to ensure sensor sensitivity, low limit of detection and high operating frequency. Although contact resistance is well understood in traditional semiconductor devices, its origins in graphene and graphene-like materials is more complex. Up until now, substantial work has not been completed towards contacting laser-induced graphene. As such, insight from the graphene literature is used as a basis for LIG-metal contacts. The optimal metal for contacting graphene is still hotly disputed, with large variability between classes of metal (physisorbing/chemisorbing) and the relative behavior of metals within those classes. This variability is caused by the large number of potential contributions to the contact resistance, including the metal deposition process, environmental interactions, metal work function, graphene layer number and resist residue.

While the direct application of these contributions to graphene-like systems may not be possible they can still provide valuable opportunities for contact resistance reduction. They are of particular concern in pristine graphene due to its low carrier concentration, lack of bulk material to pin the Fermi level and highly available surface making it highly sensitive to its environment. Therefore, external perturbations are screened more slowly than a traditional metal [39–41]. The small Density of States (DOS) and zero bandgap allow for a large change in the Fermi energy of the graphene due to external modulation [42]. This sets graphene apart from higher DOS metals, which can attenuate small charge transfers without modifying their Fermi-level.

Key in defining these interactions is the contacting metal. Two categories of metal can be used: **physisorbed** (e.g. Au, Al, Ag, Cu, Pt, Cd, In) and **chemisorbed** (e.g. Ni, Co, Ru, Pd, Ti) [43, 44]. Physisorbed metals transfer charge without rehybridizing the molecular orbitals of the underlying graphene; the electronic band structure is unmodified. Chemisorbed metals rehybridise the orbitals ($sp^2 \rightarrow sp^3$), which alters the electronic structure, opening a band gap in the previously semi-metal graphene. Au and Ni are normally used as typical physisorbing and chemisorbing metals in the literature and will be used as key demonstrators in this work.

Both types of contacting metal follow different conduction mechanisms. Physisorbed metals experience an injection barrier, while chemisorbed metals, due to bond formation, can directly inject charge into the graphene sheet.

Physisorbed metals typically have higher contact resistance than chemisorbed metals, but the chemisorbed metals cause an undesirable modulation of the contacted graphene. This can result in in-plane charge redistribution which can extend beyond the contacted region [44,45]. However, the physisorbed systems instead experience a down shifting of graphene energy levels, due to Pauli exclusion, which results in the doping of the contacted graphene [43]. The impact can be considered in terms of p/n doping and junctions. This is especially challenging due to graphene's susceptibility to be doped by surface interactions e.g. p-doping by oxygen moieties, volatile organic compounds or substrate interactions [46–48]. Depending on the metal contact and the doping interactions p-p, n-n or p-n junctions can form resulting in device asymmetry and increased contact resistance [42,47].

Chemisorbed metals have stronger (0.09-0.4 vs. 0.03-0.05 eV/carbon) and shorter range (<2.5 Å vs. >3 Å) interactions than physisorbed metals. Contaminants, which would increase the contact separation, have a larger impact on chemisorbed metal contacts [49]. Similarly, wrinkled systems see more pronounced increases in contact resistance for chemisorbed metals [50]. However, contact resistance seems to be unaffected by intrinsic structural defects (e.g. Stone-Wales defects) [46]. Additionally, physisorbed and chemisorbed metals have differing preferential sites on graphene. Chemisorbed metals prefer bridge or top sites while physisorbed metals prefer the hollow sites. This is due to the greater access to the molecular orbitals of the former and low electron density but high coordination number of the later [50]. The presence but also type of the contaminant determines its effect on the contacting metal if it has a preferred adsorption site. Graphene surface contaminants don't just act as classical resistive elements, but can also cause doping to the graphene material or interact with the contact metal unpredictably. This should be avoided as variable systems are of limited utility, while higher contact resistance but reproducible contacts can be used to produce functional devices [51].

Removing contaminant or residue is essential for good contacts to graphene, but it is not robust enough to survive traditional CMOS cleaning processes. Steps can be taken to reduce

the amount of contaminants present, such as low concentration polymer formulations [52], but cleaning steps are still essential. Low mass plasma cleaning [53], UV-Ozone cleaning [54,55] CO₂ gas flow dehydrogenation [56], Raman monitored real time laser cleaning [57] and CO₂ cluster cleaning [58] are a few of the methods trialed to balance contaminant removal and graphene damage. However, the risk of damaging the graphene isn't limited to just cleaning steps. Metallization can also alter the graphene, although this is more noticeable for chemisorbed metals [59]. This suggests the formation of metal carbides. The use of metal stacks of physisorbing/chemisorbing metals or metal alloys can allow for physisorbing metals to chemisorb avoiding the injection barrier normally seen or optimize charge injection [60–63].

These influences can be summarized into a quantum mechanical model comprised of two main parts: injection from the metal into the graphene system and transfer from the doped graphene into the channel region [64]. This is presented in terms of transmission coefficients in the Landauer-Buttiker model Equ. SI-3.1, SI-3.2. T_{MG} compiles influences restricting charge injection into the system (residue/contamination effects and equilibrium distance effects) and T_{CC} any influences affecting the injection from the contact region into the bulk of the graphene sheet (potential barriers, work functions, doping and p-junction contributions). Assuming ideal transmission coefficients the theoretical limits for top contacts is $88 \Omega\mu\text{m}$, below what is required to match current state-of-the-art [65].

$$R_c = \frac{1}{T} \frac{h\sqrt{\pi}}{4e^2\sqrt{n}} \quad (\text{SI-3.1})$$

$$T = \frac{T_{CC}T_{MG}}{(1 - (1 - T_{CC})(1 - T_{MG}))} \quad (\text{SI-3.2})$$

Where T is the transmission coefficient, n is the carrier density, T_{CC} is the transmission coefficient between the contacted graphene and the channel region, T_{MG} is the transmission coefficient between the metal and contacted graphene.

This model allows treats the contaminants as a tunnelling barrier and allows them to be treated together with equilibrium distance considerations and sheet edge terminations. It also clarifies the optimization pathway, increase T_{MG} or T_{CC} by reducing contamination, decreasing the charge injection barrier, preventing pn-junction formation, or increasing mobility. The latter two options are challenging for graphene, requiring very clean processes with low damage to

the underlying graphene and careful doping. This is challenging in graphene, and infeasible for laser-induced graphene. The first two options are more attractive.

Lower contact resistances are predicted for shorter equilibrium distances (shorter distance to tunnel). The equilibrium distance and thus contact resistance is affected by the edge termination of graphene sheets, with C terminated sheets having lower equilibrium distances than O or F terminated edges [66]. This termination can be influenced by etchants and processing conditions. Similarly the processing conditions at various steps, as has been observed in the wet/dry processing of Al contacted graphene, where T_{MG} was reduced by the formation of an interfacial oxide [67]. This suggests that careful process design can be used to reduce the contact resistance. However, this isn't the only pathway possible.

Counter-intuitively, low contaminant, high defect density graphene allows for lower contact resistance than pristine graphene. The surface defects act as edge sites or dangling bonds and allow for carbide formation, this increases T_{MG} [68]. Artificial damage to edge sites can also be used but can overly damage the surface and instead increase the contact resistance instead of decreasing it. Therefore, delicate cleaning mechanisms are still needed [47]. Comparisons of models of Ni contacted graphene in top and edge contacted geometries indicate that the side contact has a reduced contact resistance. In terms of the Landauer-Buttiker model, the top contact had $T < 0.1$, but for the edge contact $T > 0.5$. This encapsulates the negation of the tunnelling barrier due to bond formation. It also highlights that T_{MG} tends to zero for top contacts as graphene is an insulator out of plane, but it tends to 1 for carbide bonds [65]. Edge contacted structures can transfer charge directly into the sheet [69].

True edge contacts are difficult to achieve, but have been demonstrated with hBN/G/hBN stacks, demonstrating reduced contact resistance [26, 27]. This reduction in contact resistance is facilitated by dangling bonds acting as high energy sites, facilitating lower equilibrium distance and sites for chemisorption. This avoids top-surface contamination effects while allowing direct access to the graphene sheet. Artificially defined edge sites produced through targeted damage can also reduce the contact resistance. As such, partially damaging cleaning methods such as annealing can actually reduce contact resistance by facilitating numerous edge-like contacts on a planar surface [70]. More targeted methods have also been demonstrated, such as site-

specific contact region laser treatments [71], lateral cuts [72] and comb-like high perimeter structures [73]. Similarly, self-assembling metal catalyzed etch processes [59, 74], e-beam and lithographic methods have also reduced the contact resistance scaling with more densely patterned holes [75–77].

This targeted damage to the graphene to produce additional edge sites and surface defects allows for the formation of low contact resistance metal contacts. Laser-induced graphene is similar to the material formed by this targeted damage comprising of numerous interconnected sheetlets of graphene-like material, which would facilitate good chemisorption. Due to the known defective nature of graphene, its band structure is already modified from that of pristine graphene and as such shouldn't be largely modified by the metal contact. This reduces the prime limitation of chemisorbed metal contacts.

SI-3.2 Energy Dispersive X-ray (EDX) Spectroscopy and Additional Scanning Electron Microscopy

Fig. SI-3.1 is equivalent to Fig. 3.2 but presents SEM and EDX data for Au-terminated wafers in the place of the Ni shown in Fig. 3.2. We see a distinct central thinning of the polyimide, which corresponds with the first, high-powered, laser write which thinned the polyimide through ablation. Surrounding this contact plug, the high surface area LIG material is clearly observed. Of particular interest, when compared to the equivalent Ni-samples, there is minimal damage at the beam centre (Fig. SI-3.1.c). The EDX data, Fig. SI-3.1d-f, supports this view, showing a uniform distribution of Au and Si at the base of the pore. The Au layer hasn't been thinned locally, which would have resulted in the increased Si signal in that region, as seen for Ni, Fig. 3.2f. This is likely caused by several factors including the differing reflectivities and adhesion properties of the base metals but more critically their chemical stabilities.

As will be discussed in more depth in the Appendix SI-3.3, in regards to the Raman spectroscopy. As Ni tends to form carbides and oxides more easily than gold is likely the cause of the damage observed. This would locally disrupt the Ni metal layer exposing the SiO₂, as observed in the EDX map. It is worth noting that the carbon signal is not zero from the base of

the “keyhole” sites, instead just lower intensity than the surrounding regions. This agrees with the Raman spectroscopy data (Figure 3.3) and suggests a thin film of with significant carbon content is present.

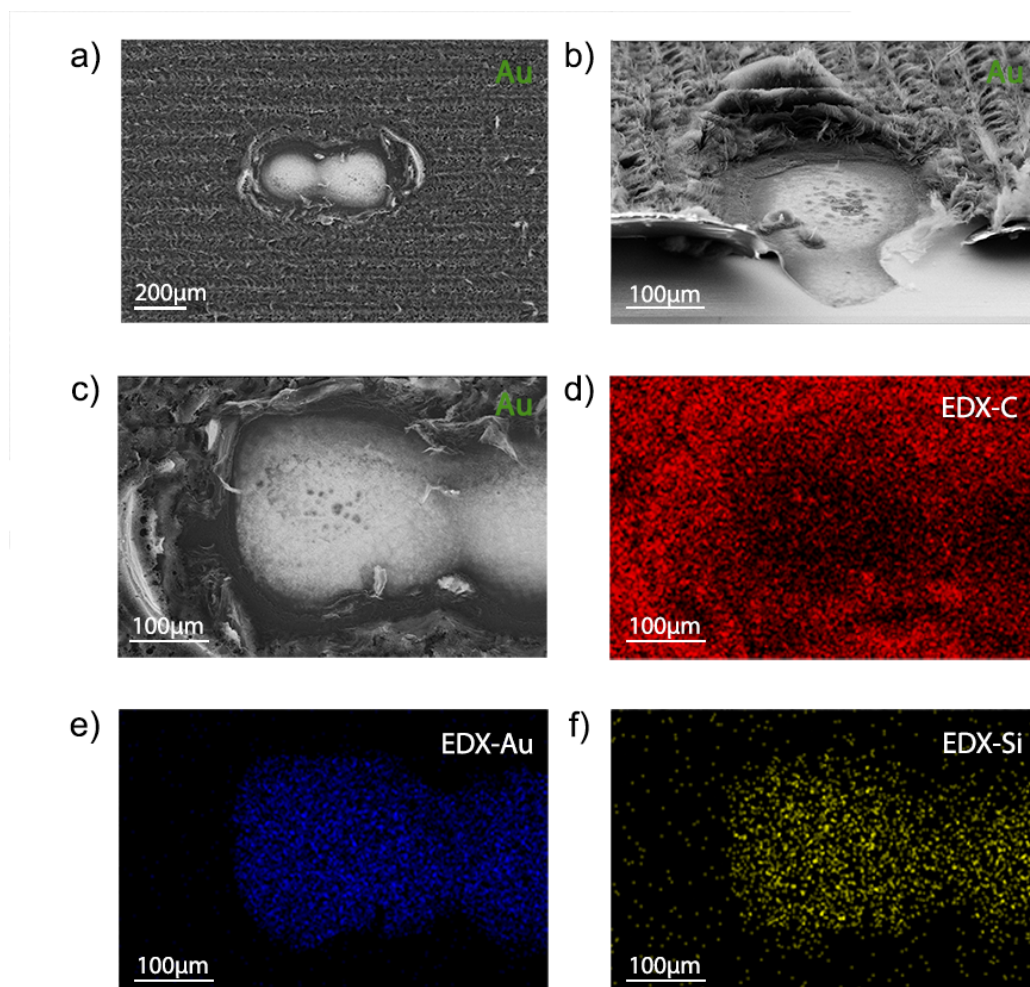


Figure SI-3.1: SEM data: a) Planar SEM of keyhole contact plug formed by 2-step local laser ablation of polyimide deposited on an Au-terminated Si/SiO₂ wafer. b) Cross-sectional SEM of mechanically cleaved LIG contact plug on Au-terminated wafer after the second laser write. c) Higher magnification view of a contact plug following the second laser step on a Au-terminated wafer. d-f) Energy Dispersive X-Ray spectroscopy maps of a contact plug following Lase#2 on a Au-terminated wafer demonstrating spatially defined abundance of d): Carbon, e): Gold and f): Silicon.

Figure SI-3.2 presents additional SEM micrographs for both Lase#1 and Lase#2 cross sectioned material. Flake-like stacks of layers of LIG-like material is observed in the wall region in both cases, with increased cross-linkage after Lase#2. The damage caused by Lase#2 to the base material is clear when comparing SI-3.2c and SI-3.2f; where regions of small, flake-like material are replaced with poorly connected clusters with reduced porosity. The edge region,

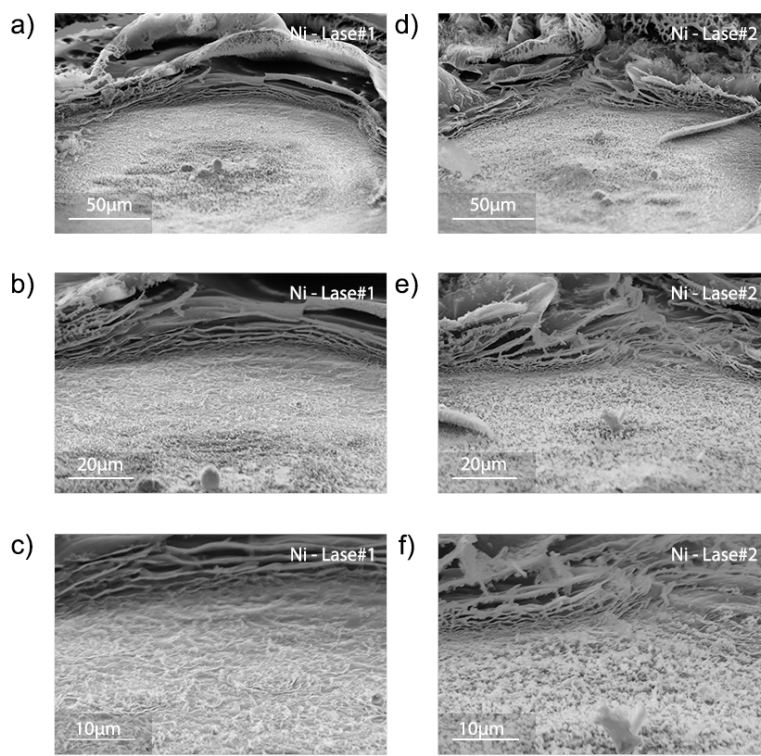


Figure SI-3.2: Cross-sectional SEM data of a cleaved Ni-terminated device showing the morphology of the base and wall of the contact plug after: a-c) Lase#1 (30 W, 18mm/s) and d-f) Lase#2 (3.7 W, 200mm/s).

where the wall meets the base, is of particular interest. It shows good connectivity to both the base and wall regions, although mediated through flake-like strands. This continuum of morphologies corresponds well with the distinct Raman behaviors shown in Fig. 3.3.

Considering this alongside the previous discussion about the damaged Ni-surface (Figure 3.2), originating from carbide formation, clarifies the distinction seen in Figure SI-3.4, whereby the quality of graphene on Au after a single write of Lase#1, is closer to that of high quality LIG than that of Ni. The carbide formation damages/limits the quality of LIG produced at the base of the pore. The convergence of their Raman properties after Lase#2 indicates the increased damage caused by further lasing a thin layer of delicate material.

SI-3.3 Additional Raman Spectra

The Raman reported in the body of this work focuses on LIG fabricated from polyimide deposited on Ni-terminated wafers, but equivalent analysis was completed on Au-terminated samples. As

has been previously noted, Raman spectroscopy of laser-induced graphene is highly variable, as it is very dependent on local defects and LIG has numerous edge defects throughout. As such it is necessary to consider the full dataset and present a representative sample. Included here, Fig SI-3.3, are representative spectra of the LIG top surface for both Ni and Au. Both samples represent high quality LIG, with extractable D' peaks and sharp, deconvolved D and G peaks.

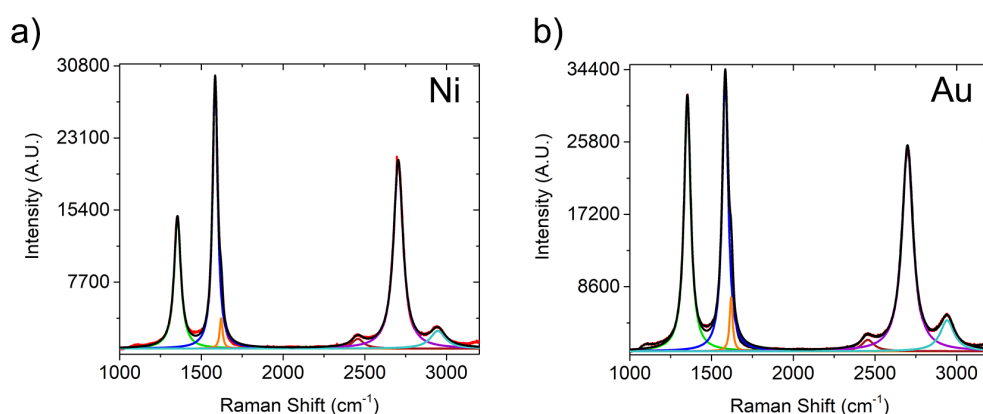


Figure SI-3.3: Representative Raman spectra of LIG material formed from polyimide deposited on a) Ni-terminated and b) Au-terminated wafer stacks.

Also, worth discussion is the variation of the base of the plug after the first high-power laser step (Lase#1), compared to its double written equivalent. These spectra shown in Fig. SI-3.4 were produced on adjacent plugs from the same first writing step, with only one experiencing a secondary write. The difference between Ni and Au is clear. Ni doesn't vary significantly between the first and the second write. The Au based sample transforms for a nearly ideal graphene-like Raman spectrum to a more graphitic spectrum. This is suggestive of a substrate dependent process. This is already hinted at in the SEM and EDX analysis, as the Ni samples experience more damage to the base metal than the Au, which was ascribed to the formation of Ni oxides and carbides during the Lasing process. The difference in the quality of material produced at the base of the plug after a single write between the Ni and Au samples further supports this view. The high defect concentration shown on Ni-based devices could correspond to graphitic material that have had their sp^2 structure partially hybridized to sp^3 due to bonding with Ni. Fig. SI-3.4c does not show this behavior, as Au is chemically stable. This corresponds to chemi-/physi-sorption nature of Ni/Au respectively.

On both metal-based devices the second laser write damages the base metal graphitic material,

to an equivalent degree, Fig. SI-3.4b,d, with Au-based samples losing the sharp, well defined peak shapes of graphene-like material. In both cases this corresponds with material that has been damaged by laser ablation.

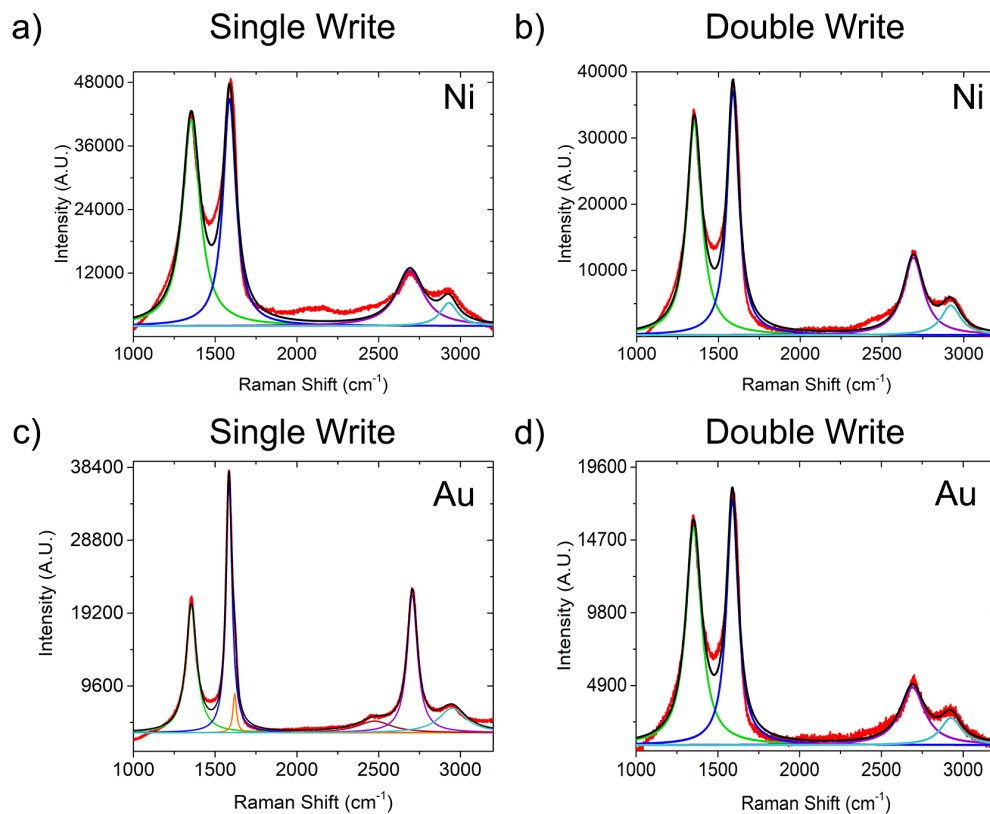


Figure SI-3.4: Representative Raman spectra for plug material LIG material on top of Ni (a, b) and Au (c, d) after a single write, i.e. Lase#1 step (a, c); and double-write step (b, d) i.e. Lase#1 & Lase#2.

Table SI-3.1: Extracted Lorentzian fit parameters from data shown in Fig. SI-3.3, Raman spectra of Ni and Au terminated wafer stacks and Fig. SI-3.4, Raman spectra of base of plugs following Lase#1 and Lase#2 steps.

	Top Surface LIG (Ni wafer, Lase#2)			Top Surface LIG (Au Wafer, Lase#2)		
	Peak Pos (cm ⁻¹)	FWHM (cm ⁻¹)	A/A _G	Peak Pos (cm ⁻¹)	FWHM (cm ⁻¹)	A/A _G
D	1354	60	0.65	1352	49	1.03
G	1584	370	n/a	1584	44	n/a
D'	1621	21	0.06	1620	22	0.1
2D	2704	69	1.30	2699	81	1.38
	Plug Base (Ni, Lase#1)			Plug Base (Au, Lase#1)		
	Peak Pos (cm ⁻¹)	FWHM (cm ⁻¹)	A/A _G	Peak Pos (cm ⁻¹)	FWHM (cm ⁻¹)	A/A _G
D	1354	130	1.23	1355	79	0.89
G	1588	96	n/a	1585	45	n/a
D'	Absent			1620	26	0.09
2D	2691	200	0.51	2705	76	0.92
	Plug Base (Ni, Lase#1 & Lase#2)			Plug Base (Au, Lase#1 & Lase#2)		
	Peak Pos (cm ⁻¹)	FWHM (cm ⁻¹)	A/A _G	Peak Pos (cm ⁻¹)	FWHM (cm ⁻¹)	A/A _G
D	1352	110	1.11	1352	115	1.18
G	1589	86	n/a	1589	87	n/a
D'	Absent			Absent		
2D	2692	150	0.55	2690	180	0.49

SI-3.4 Calculation of Contact Resistance

In the lollipop structures there is an unaccounted-for resistance component due to the contact point being outside the channel. This is due to the zero point of the channel being outside of the contacting pad. This is a non-negligible component, so must be compensated for, to investigate the influence of multiple contacting plugs.

Recall the general length dependence of resistance:

$$\begin{aligned}
 R &= \frac{\rho L}{A} + R_C \\
 &= \frac{R_{sh}}{W} L + R_C
 \end{aligned}$$

This deviates from the traditional ohmic dependence by allowing for a constant term stemming from contact resistance or other deviations from the ideal ohmic material.

$$R_C = R_{probe+leads} + aR_{probe-LIG} + b(R_{probe-metal} + R_{metal-LIG} + R_{plug}) + R_{\Delta} + R_{spread} + R_{oth}$$

$$R_C \approx 0 + aR_{probe-LIG} + b(0 + R_{metal-LIG} + R_{plug}) + R_{\Delta} + R_{spread} + R_{oth}$$

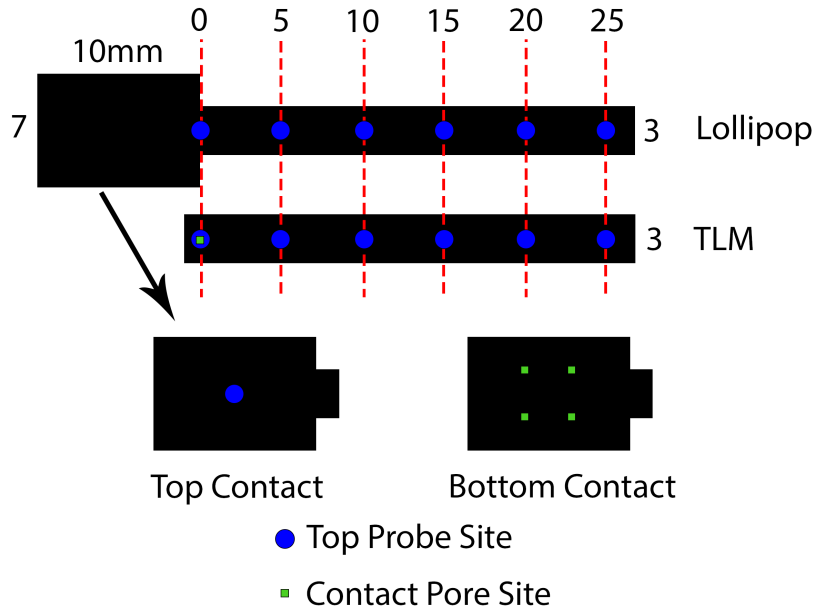


Figure SI-3.5: Patterns and contact points for “lollipop” and traditional TLM test structures. Top contact refers to a probe station probe contacting the material from above, while the bottom contact uses an etched plug to contact to the buried which is contacted with a probe externally to the laser-induced graphene structure.

where $R_{(probes+leads)}$ is the resistance contribution from the probes and leads of the probe station, $R_{(probe-LIG)}$ is the contact resistance between the probe and top surface LIG, $R_{(probe-metal)}$ is the contact resistance between the probe and the exposed metal, $R_{(metal-LIG)}$ is the contact resistance between the base metal and the LIG plug, R_{plug} is the resistance associated with travelling up through the contact plug, R_{Δ} is the unaccounted for resistance contribution associated with changing device geometry in the contact pad, R_{spread} is the spreading resistance associated with travelling from the channel region into the contact region and R_{oth} accounts for any unknown contribution not considered explicitly. In general, $a=1$ or 2 depending on whether it is bottom or top contacted to account for the number of probe-LIG contacts present. Similarly, when bottom contacted, $b=1$ or 0 when top contacted scaling the contribution of the probe-metal, metal-LIG and LIG plug contributions accordingly. The contributions of the probe and lead resistance and probe-metal resistance are assumed to be essentially zero relative to the magnitude of the LIG-based contributions, simplifying the expression. As such they will be neglected going forward. Together $R_{\Delta} + R_{spread} + R_{oth}$ are used to describe the unaccounted-for resistance in the lollipop structure. In a traditional TLM structure these terms take a value of 0 . In further

steps these terms will be abbreviated to R_{Δ} as it should be the largest contributor.

This leaves us with the simplified approximation of c:

$$R_c = aR_{probe-LIG} + b(R_{metal-LIG} + R_{plug}) + R_{\Delta}$$

These correspond to sheet resistances of ≈ 60 - 100 Ohm/sq. which correspond to that seen on oxide (≈ 75 Ohm/sq.) These sheet resistances, although high relative to what can be achieved on commercially available ≈ 100 μm thick polyimide, which can now be reduced as low as ≈ 6 ohm/sq. [9] it is produced on only 17.5 μm of spin coated material. Further optimization of the precursor and process could further reduce this.

Taking the intercept terms in each case we see:

$$C_{Top}^L = 2R_{Probe-LIG} + R_{\Delta}$$

$$C_{Bot}^L = R_{Probe-LIG} + R'_{\Delta} + R_{Plug} + R_{Metal-LIG}$$

$$C_{Top}^T = 2R_{Probe-LIG}$$

$$C_{Bot}^T = R_{Probe-LIG} + R_{Plug} + R_{Metal-LIG}$$

Firstly, considering the bar system for Au-contacted LIG:

Estimating the probe-LIG contact resistance:

$$C_{Top}^T = 2R_{Probe-LIG} = 43.6 \Omega$$

$$R_{Probe-LIG} \approx 22 \Omega$$

Estimating the base plug contact resistance:

$$C_{Bot}^T = R_{Probe-LIG} + R_{Plug} + R_{Metal-LIG} = 367.7 \Omega$$

The Contributions of $R_{Plug} + R_{Metal-LIG}$ can be treated as a single element as they occur together and cannot be separated in this calculation, as such they will be renamed $R_c^{T-Metal-LIG} =$

$$R_{plug} + R_{Metal-LIG}.$$

$$R_{probe-LIG} + R_c^{T-Metal-LIG} = 367.7 \Omega$$

If we assume that the $R_{Probe-LIG}$ in the top contacted geometry is similar to its contribution in bottom geometry, then:

$$R_c^{T-Metal-LIG} = 367.7\Omega - R_{Probe-LIG}$$

$$R_c^{T-Metal-LIG} = 367.7\Omega - 22\Omega = 345.7 \Omega$$

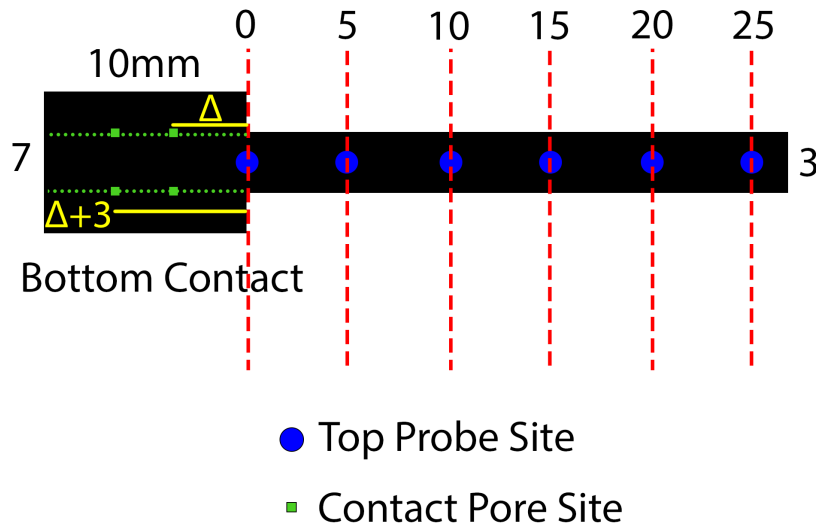


Figure SI-3.6: Lollipop electrode structure demonstrating unaccounted for channel length, Δ .

Considering the lollipop electrode system:

$$C_{Top}^L = 2R_{Probe-LIG} + R_{\Delta}$$

$$C_{Bot}^L = R_{Probe-LIG} + R_{Metal-LIG} + R_{Plug} + R_{\Delta}$$

$$= R_{Probe-LIG} + R_c^{L-Metal-LIG} + R_{\Delta}$$

Assuming that $R_{Probe-LIG}^T \approx R_{Probe-LIG}^L$, then an estimate for the unaccounted-for resistance can be found:

$$\begin{aligned}
R_{\Delta} &= C_{Top^L} - 2R_C^T \\
&\approx 179.5 \, \Omega - 44 \, \Omega \\
&\approx 135.5 \, \Omega
\end{aligned}$$

$$R_c^{L-Metal-LIG} = C_{Bot}^L - R_{\Delta}^- R_{Pore-LIG}^L$$

Then again assuming that $R_{Pore-LIG}^T \approx R_{Pore-LIG}^L$ and using the estimate found for R_{Δ} :

$$\begin{aligned}
R_c^{L-Metal-LIG} &\approx C_{Bot}^L - R_{\Delta}^- R_{Pore-LIG}^T \\
&= 210.1 - 135.5 - 22 \\
&\approx 53 \, \Omega
\end{aligned}$$

This gives us an estimate for the contact resistance of one metal-plug (345.7 Ω) and an estimate for four plugs (53 Ω)

Recalling that for a parallel path:

$$1/R_{tot} = \sum 1/R_1 + 1/R_2 + \dots 1/R_n$$

Then assuming that all four plugs contribute equally:

$$R_{tot} = 345.7/4 = 86.4\Omega$$

This is in good agreement with what we saw for our four-plug system ($53\Omega \approx 86.4\Omega$)

This above calculation was carried out in the case of Au, following the same method an estimate for Ni can be reported. Single plug - 158.7 Ω , 4 plug - 32.6 Ω , estimate for 4 plug - 39.7 Ω . The value of the measured and estimated 4-plug contact resistances are also in good agreement for Ni (32.6 $\Omega \approx 39.6 \, \Omega$).

SI-3.5 Contact Resistance Area Dependence

Contact resistance (R_C) is the additional resistance introduced to a system from the electrical contact and is independent of the channel. In the standard transfer line measurements (TLM) conducted in this work, it is half the intercept value ($R = \rho L/A + 2R_c$). However, the asymmetric structures (schematically shown in Fig.SI-3.7) demonstrated in this work have two different contacts; a probe-LIG contact and a probe-metal-LIG contact, each of which would have its own R_c . Conducting a TLM using both probe-LIG contacts we can find its R_c . Subtracting R_c from the asymmetric contact intercept estimates R'_c , the contact resistance of the probe-metal-LIG contact ($\approx$ metal-LIG contact).

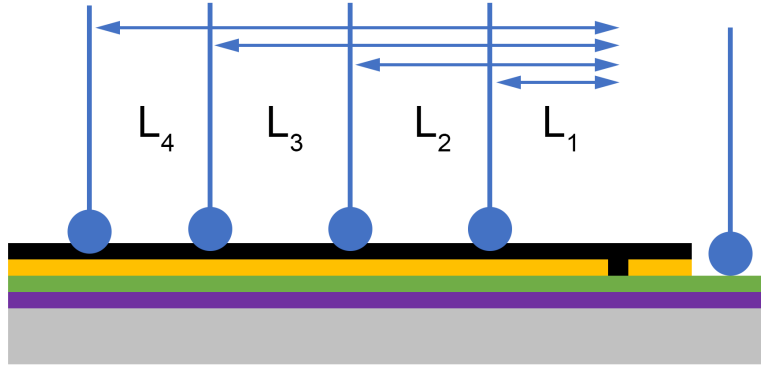


Figure SI-3.7: Transfer line measurement spacing schematic for asymmetric contact geometry.

Unlike standard resistance expressions the contact resistance does depend on the length of the material as it describes an interface. As such the contact resistance scales areally: $R_c = \rho_c/A = \frac{\rho_c}{WL}$ where A is the area of a contact, W (perpendicular to the current travel direction) is the width, L is its length of the contact (parallel to the current travel direction) and ρ_c is the contact resistivity. In semiconductor systems, due to the orders of magnitude difference in resistivities the current path favours the metal, travelling through the metal as far as possible before entering the semiconductor. Only a small region of the sample area participates in the conduction due to current crowding (this is referred to as the transfer length $L_T = \sqrt{\frac{\rho_c}{R_{sh}}}$). In this situation, regardless of how long the contact region is, only the last L_T meaningfully contributes to the conduction path. Therefore, for an areally contacted metal-semiconductor interface, the

contact resistance only depends on the width of the contact ($R_c \propto \frac{1}{WL}$), if $L \geq L_T$ (or $R_C \propto \frac{1}{WL}$ if the resistivities of the materials are similar).

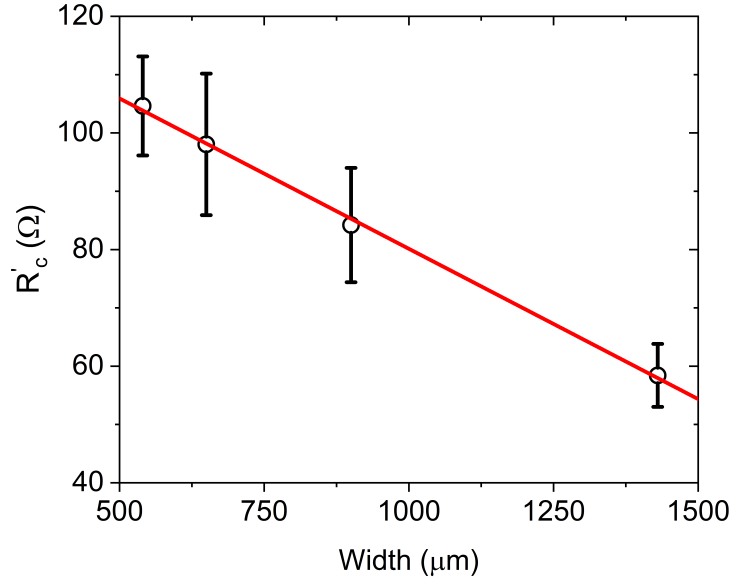


Figure SI-3.8: Contact width dependence of contact resistance determined from a series of transfer line measurements on Au terminated Si/SiO₂ wafer.

However, as demonstrated in Fig. SI-3.8, the dependence of contact resistance for the keyhole contacted LIG structures is directly proportional to the width of the contact (estimated from SEM, Fig SI-3.9), under these formation conditions. This does not correspond to areal scaling, as outlined, rather suggesting a dependence on the contact perimeter. The SEM micrographs (Fig. 3.2) coupled with the Raman spectra (Fig. 3.3) correspond to a thin layer of graphene-like material. While this layer would limit the direct exposure of the metallic layer it would prevent significant current flow. Instead, the current path would access the graphene-like walls near the perimeter of the base, the least resistive path.

Although the exact current path cannot be directly determined, we can estimate the resistivity of the contacting region between the metal and the top surface to an order of magnitude based on the perimeter scaling and SEM micrographs (Fig. SI-3.9). Assuming the current path extends through a $\approx 25 \mu\text{m}$ region on either side that defines the region between the base and the actual wall (shown in red). If this is consistent and the contact length is $250 \mu\text{m}$, width is $1400 \mu\text{m}$ and height is $17 \mu\text{m}$. Then from $R = \rho L/A$, where $A = (250 \times 1400) - (200 \times 1350) = 80,000 \mu\text{m}^2$, $L=17 \mu\text{m}$, and $R \approx 60 \Omega$: $\rho \approx 0.3 \Omega\text{m}$.

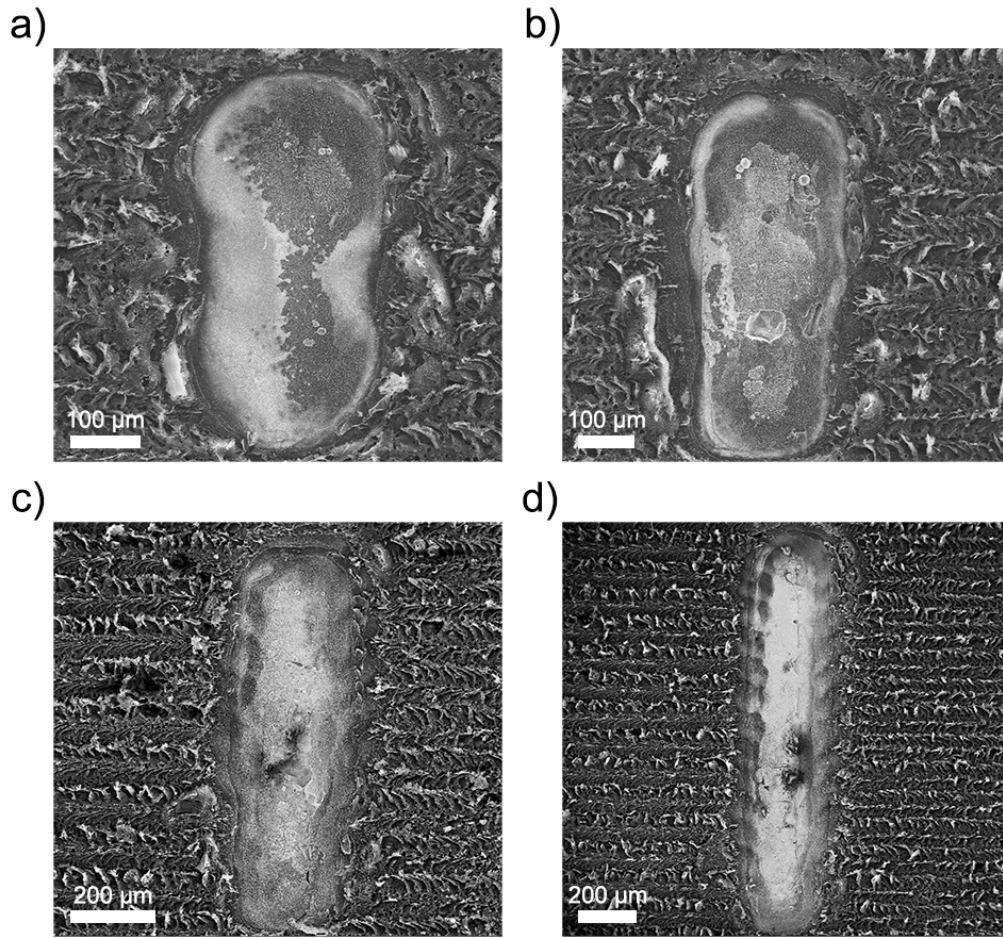


Figure SI-3.9: Scanning electron micrographs of contact keyholes of differing lengths: a) $\approx 250 \times 550 \mu\text{m}$, b) $\approx 250 \times 650 \mu\text{m}$, c) $\approx 250 \times 900 \mu\text{m}$, d) $250 \times 1450 \mu\text{m}$.

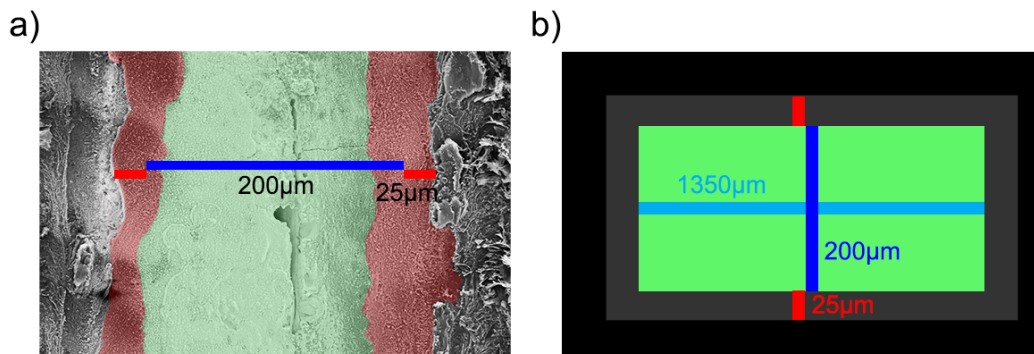


Figure SI-3.10: a) False coloured SEM micrograph demonstrating estimates for the central contact region (green), the base-wall interface region (red), and the surrounding top surface material (uncoloured), b) schematic of the corresponding contact dimensions.

SI-3.6 Thickness Dependence

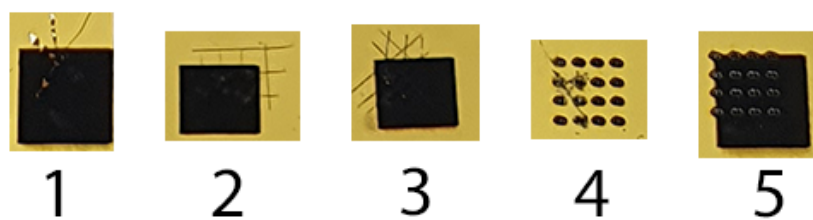


Figure SI-3.11: Attempted mechanical (1-3) and laser (4-5) bottom contacting treatments

Initial contacting approaches involved the mechanical scoring of the polyimide film to provide a pathway towards the base metal to convert in subsequent laser conversion. Differing line densities and applied force demonstrated that more numerous deeper scores resulted in lower contact resistances. However, as they were formed by mechanical scratching with a scalpel, they had poor reproducibility. Instead, self-alignable, laser methods were used to imitate the mechanical thinning step followed by the material top cap. This highlights that thicker polyimide layers can be processed to allow for contact to be achieved, while electrically isolating the top cap outside the contact region.

However, the contacting method isn't the only significant factor, there is a clear substrate thickness dependence in the formation of high quality LIG on wafer. Although not the focus of this work there is likely an additional dependence on the specific polymer formulation and processing conditions, requiring individual optimizations. This thickness dependence was demonstrated using a single spin cast and a double spin cast of the same polyimide precursor (PI-5878G) and cure on raw Si wafers. After curing these produced films of $\sim 8.5\mu\text{m}$ and $\sim 17.5\mu\text{m}$ respectively.

The formation conditions required to produce LIG on each of these substrates were vastly different, requiring higher laser powers for the thinner film. The mechanism behind this is suspected to be a combination of parasitic cooling of the irradiated polymer with the wafer acting as a heat sink, and the polymer layer being too thin to absorb sufficient energy from the laser source. The lowest resistance demonstration on the thin film (formed using 6 W laser Power, 175 mm/s scan speed, 20 lines/mm y-line density) exceeded 1 kOhm/Sq. Raman analysis showed it was a highly defective graphitic material. In contrast, the thicker film produced from the double

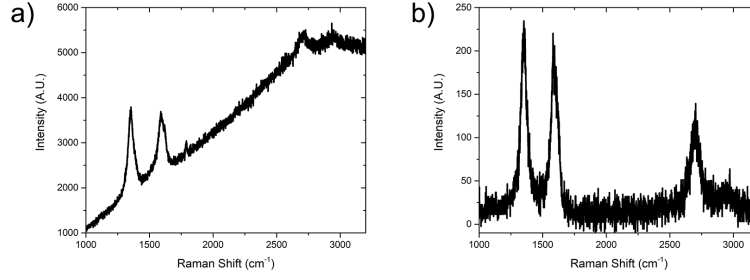


Figure SI-3.12: a) Single thickness polyimide on wafer LIG Raman response. b) Double thickness Polyimide on Wafer LIG Raman response.

spin coating, produced high quality LIG, as can be seen from its Raman spectrum, at more moderate laser powers (3.75 W laser power 205 mm/s scan speed, 20 lines/mm y-line density, 0.4 mm z height) producing sheet resistances of $\sim 75 \text{ Ohm/Sq}$.

Further insight can be gained from the formation of parallel plate capacitor structures on double-thickness polyimide-metal-oxide-Si stacks. Taking the slope of figure SI-3.13 is $\sim 3.8 \mu\text{F/m}^2$ and ϵ_r is approximately 3 for polyimide, then d is approximately $7 \mu\text{m}$, using equations Equ. SI-3.3 and SI-3.4. This suggests that there is approximately $7 \mu\text{m}$ of unconverted polyimide remaining of the original $17.5 \mu\text{m}$. The other $10 \mu\text{m}$ of which has either been ablated away or converted into LIG. This insulates the surface LIG from the base metal without any pinholes or leakage paths, present in the -20, 20 V potential sweep.

This adds an additional dimension to the discussion, the polyimide must also be sufficiently thick to allow for full conversion, given that $\sim 10 \mu\text{m}$ of polyimide is converted in the double-coated, on metal system, it is likely that the $8.5 \mu\text{m}$ is not thick enough to take full advantage of the conversion. Further, if the polyimide is too thin then the highly localized heating required for the polyimide conversion to LIG isn't possible as it is no longer thermally isolated as would be the case in standard thicker polyimide systems. This is likely the reason that higher laser powers are needed, to balance the substrate assisted cooling.

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (\text{SI-3.3})$$

$$d = \epsilon_0 \epsilon_r \frac{A}{C} \quad (\text{SI-3.4})$$

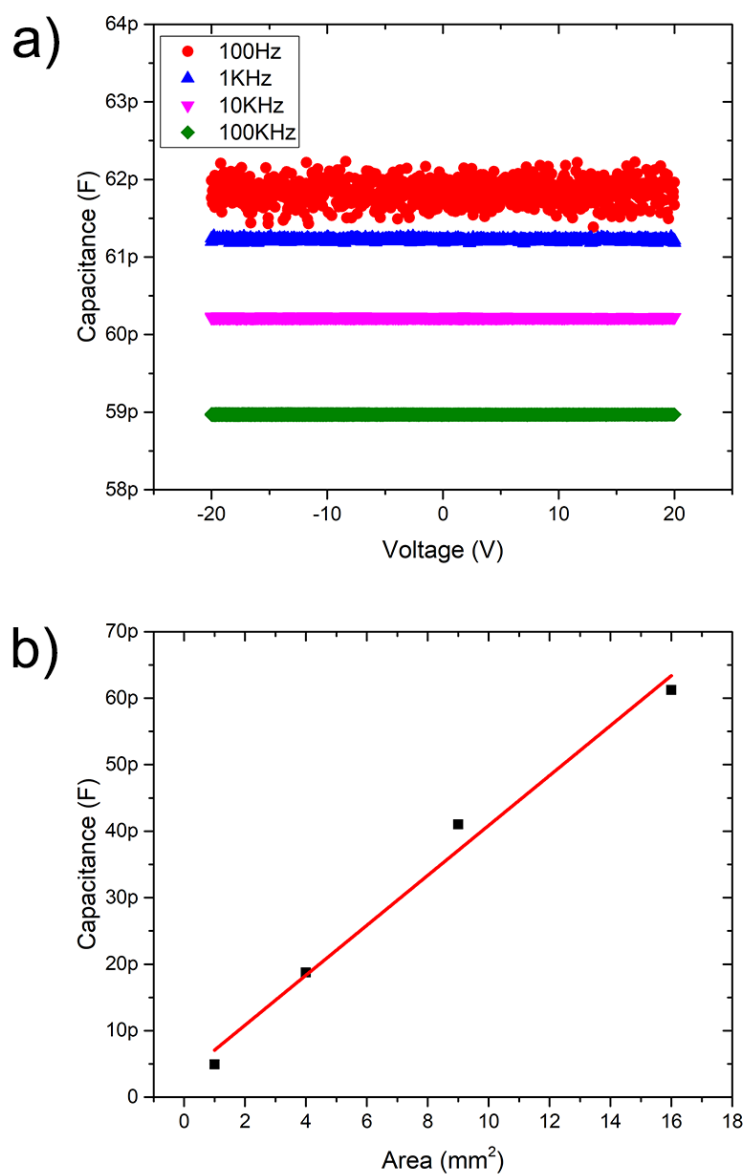


Figure SI-3.13: a) -20, 20 V potential sweep of $4 \times 4 \text{ mm}$ LIG square on Au base metal without contacting plugs at different frequencies. b) Parallel plate capacitance of LIG-Base metal squares varying with LIG square area.

SI-3.7 Electrochemistry Data

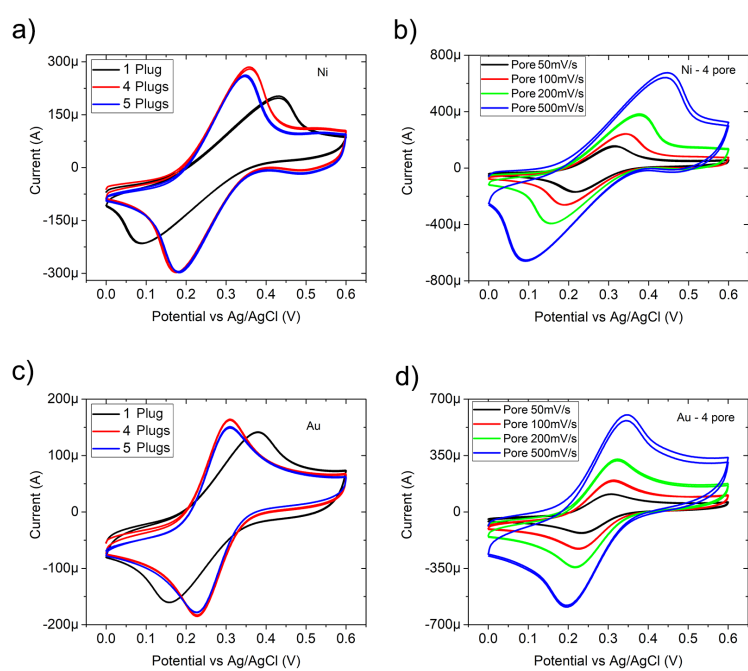


Figure SI-3.14: Compiled Cyclic Voltammograms of (a, b) Ni terminated-, (c, d) Au terminated-wafer stacks for both scaling number of plugs and channel lengths.

BIBLIOGRAPHY

- [1] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, and J. M. Tour, "Laser-induced porous graphene films from commercial polymers," *Nature Communications*, vol. 5, p. 5714, dec 2014.
- [2] M. G. Stanford, K. Yang, Y. Chyan, C. Kittrell, and J. M. Tour, "Laser-induced graphene for flexible and embeddable gas sensors," *ACS Nano*, vol. 13, no. 3, p. 3474–3482, 2019.
- [3] M. Burke, C. Larrigy, E. Vaughan, G. Paterakis, L. Sygellou, A. J. Quinn, G. Herzog, C. Galiotis, and D. Iacopino, "Fabrication and electrochemical properties of three-dimensional (3d) porous graphitic and graphenelike electrodes obtained by low-cost direct laser writing methods," *ACS Omega*, vol. 5, no. 3, p. 1540–1548, 2020.
- [4] M. Athanasiou, N. Samartzis, L. Sygellou, V. Dracopoulos, T. Ioannides, and S. N. Yannopoulos, "High-quality laser-assisted biomass-based turbostratic graphene for high-performance supercapacitors," *Carbon*, vol. 172, p. 750–761, 2021.
- [5] M. Yuan, F. Luo, Y. Rao, J. Yu, Z. Wang, H. Li, and X. Chen, "Swcnt-bridged laser-induced graphene fibers decorated with mno₂ nanoparticles for high-performance flexible micro-supercapacitors," *Carbon*, vol. 183, p. 128–137, 2021.
- [6] M. R. Bobinger, F. J. Romero, A. Salinas-Castillo, M. Becherer, P. Lugli, D. P. Morales, N. Rodríguez, and A. Rivadeneyra, "Flexible and robust laser-induced graphene heaters photothermally scribed on bare polyimide substrates," *Carbon*, vol. 144, p. 116–126, 2019.
- [7] Y. Dong, S. C. Rismiller, and J. Lin, "Molecular dynamic simulation of layered graphene clusters formation from polyimides under extreme conditions," *Carbon*, vol. 104, pp. 47–55, 2016.
- [8] R. Murray, M. Burke, D. Iacopino, and A. J. Quinn, "Design of experiments and optimization of laser-induced graphene," *ACS Omega*, vol. 6, p. 16736–16743, Jul 2021.
- [9] A. Minhas-Khan, S. Nambi, and G. Grau, "Low-resistance laser-induced graphitic carbon by maximizing energy delivery and pulse overlap," *Carbon*, vol. 181, p. 310–322, 2021.
- [10] H. Wahab, V. Jain, A. S. Tyrrell, M. A. Seas, L. Kotthoff, and P. A. Johnson, "Machine-learning-assisted fabrication: Bayesian optimization of laser-induced graphene patterning using in-situ raman analysis," *Carbon*, vol. 167, p. 609–619, 2020.
- [11] R. Ye, Y. Chyan, J. Zhang, Y. Li, X. Han, C. Kittrell, and J. M. Tour, "Laser-Induced Graphene Formation on Wood," *Advanced Materials*, vol. 29, no. 37, 2017.
- [12] Y. Chyan, R. Ye, Y. Li, S. P. Singh, C. J. Arnusch, and J. M. Tour, "Laser-Induced Graphene by Multiple Lasing: Toward Electronics on Cloth, Paper, and Food," *ACS Nano*, vol. 12, pp. 2176–2183, mar 2018.
- [13] X. Han, R. Ye, Y. Chyan, T. Wang, C. Zhang, L. Shi, T. Zhang, Y. Zhao, and J. M. Tour, "Laser-Induced Graphene from Wood Impregnated with Metal Salts and Use in Electrocatalysis," *ACS Applied Nano Materials*, vol. 1, no. 9, pp. 5053–5061, 2018.
- [14] Y. Rao, M. Yuan, F. Luo, Z. Wang, H. Li, J. Yu, and X. Chen, "One-step laser fabrication of phosphorus-doped porous graphene electrodes for high-performance flexible microsupercapacitor," *Carbon*, vol. 180, p. 56–66, 2021.
- [15] Z. Wan, M. Umer, M. Lobino, D. Thiel, N. T. Nguyen, A. Trinchì, M. J. Shiddiky, Y. Gao, and Q. Li, "Laser induced self-n-doped porous graphene as an electrochemical biosensor for femtomolar mirna detection," *Carbon*, vol. 163, p. 385–394, 2020.
- [16] Z. Peng, R. Ye, J. A. Mann, D. Zakhidov, Y. Li, P. R. Smalley, J. Lin, and J. M. Tour, "Flexible boron-doped laser-induced graphene microsupercapacitors," *ACS Nano*, vol. 9, no. 6, p. 5868–5875, 2015.
- [17] L. X. Duy, Z. Peng, Y. Li, J. Zhang, Y. Ji, and J. M. Tour, "Laser-induced graphene fibers," *Carbon*, vol. 126, p. 472–479, Jan 2018.

- [18] M. Kim, K. Yang, Y. S. Kim, J. C. Won, P. Kang, Y. H. Kim, and B. G. Kim, "Laser-induced photothermal generation of flexible and salt-resistant monolithic bilayer membranes for efficient solar desalination," *Carbon*, vol. 164, p. 349–356, 2020.
- [19] T. Chu and Z. Chen, "Understanding the electrical impact of edge contacts in few-layer graphene," *ACS Nano*, vol. 8, no. 4, pp. 3584–3589, 2014.
- [20] L. Li, J. Zhang, Z. Peng, Y. Li, C. Gao, Y. Ji, R. Ye, N. D. Kim, Q. Zhong, Y. Yang, H. Fei, G. Ruan, and J. M. Tour, "High-performance pseudocapacitive microsupercapacitors from laser-induced graphene," *Advanced Materials*, vol. 28, no. 5, p. 838–845, 2016.
- [21] L. Yang, N. Yi, J. Zhu, Z. Cheng, X. Yin, X. Zhang, H. Zhu, and H. Cheng, "Novel gas sensing platform based on a stretchable laser-induced graphene pattern with self-heating capabilities," *Journal of Materials Chemistry A*, vol. 8, no. 14, pp. 6487–6500, 2020.
- [22] J. Zhu, Z. Hu, C. Song, N. Yi, Z. Yu, Z. Liu, S. Liu, M. Wang, M. G. Dexheimer, J. Yang, and H. Cheng, "Stretchable wideband dipole antennas and rectennas for rf energy harvesting," *Materials Today Physics*, vol. 18, p. 100377, May 2021.
- [23] J. Zhu, S. Liu, Z. Hu, X. Zhang, N. Yi, K. Tang, M. G. Dexheimer, X. Lian, Q. Wang, J. Yang, J. Gray, and H. Cheng, "Laser-induced graphene non-enzymatic glucose sensors for on-body measurements," *Biosensors and Bioelectronics*, vol. 193, p. 113606, Dec 2021.
- [24] F. Léonard and A. A. Talin, "Electrical contacts to one- and two-dimensional nanomaterials," *Nature Nanotechnology*, vol. 6, no. 12, pp. 773–783, 2011.
- [25] W. S. Leong, C. T. Nai, and J. T. L. Thong, "What does annealing do to metal–graphene contacts?," *Nano Letters*, vol. 14, p. 3840–3847, Jul 2014.
- [26] B. Krishna Bharadwaj, D. Nath, R. Pratap, and S. Raghavan, "Making consistent contacts to graphene: Effect of architecture and growth induced defects," *Nanotechnology*, vol. 27, no. 20, p. 1–6, 2016.
- [27] H. Pandey, M. Shaygan, S. Sawallich, S. Kataria, Z. Wang, A. Noculak, M. Otto, M. Nagel, R. Negra, D. Neumaier, and M. C. Lemme, "All CVD Boron Nitride Encapsulated Graphene FETs with CMOS Compatible Metal Edge Contacts," *IEEE Transactions on Electron Devices*, vol. 65, no. 10, pp. 4129–4134, 2018.
- [28] A. C. Ferrari and D. M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of graphene," *Nature Nanotechnology*, vol. 8, no. 4, pp. 235–246, 2013.
- [29] A. Eckmann, A. Felten, A. Mishchenko, L. Britnell, R. Krupke, K. S. Novoselov, and C. Casiraghi, "Probing the nature of defects in graphene by Raman spectroscopy," *Nano Letters*, vol. 12, no. 8, pp. 3925–3930, 2012.
- [30] A. C. Ferrari and J. Robertson, "Interpretation of raman spectra of disordered and amorphous carbon," *Phys. Rev. B*, vol. 61, no. 20, p. 14 295, 2000.
- [31] H. O. Pierson, *Applications of Refractory Carbides and Nitrides*. Noyes Publications, 1996.
- [32] D. Iacopino, E. Vaughan, C. Larrigy, M. Burke, L. Sygellou, A. J. Quinn, C. Galiotis, and D. Iacopino, "Visible laser scribing fabrication of porous graphitic carbon electrodes: Morphologies, electrochemical properties, and applications as disposable sensor platforms," *ACS Applied Electronic Materials*, vol. 2, p. 3279–3288, Oct 2020.
- [33] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, and J. L. Dempsey, "A practical beginner's guide to cyclic voltammetry," *Journal of Chemical Education*, vol. 95, p. 197–206, Feb 2017.
- [34] R. S. Nicholson and I. Shain, "Correction: Theory of stationary electrode polarography: Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems," *Analytical Chemistry*, vol. 36, no. 7, p. 1212, 1964.
- [35] R. J. Klingler and J. K. Kochi, "Electron-transfer kinetics from cyclic voltammetry. quantitative description of electrochemical reversibility," *Journal of Physical Chemistry*, vol. 85, no. 12, p. 1731–1741, 1981.
- [36] I. Lavagnini, R. Antiochia, and F. Magno, "An extended method for the practical evaluation of the standard rate constant from cyclic voltammetric data," *Electroanalysis*, vol. 16, no. 6, p. 505–506, 2004.

- [37] S. Menolasina, "Electrochemical studies of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ on gold ultramicroelectrodes varying the concentrations of K^+ as supporting electrolyte," *Revista Técnica de la Facultad de Ingeniería Universidad del Zulia*, vol. 28, no. 2, p. 159–168, 2005.
- [38] K. N. Parrish and D. Akinwande, "Impact of contact resistance on the transconductance and linearity of graphene transistors," *Applied Physics Letters*, vol. 98, no. 18, 2011.
- [39] A. Venugopal, A. Pirkle, R. M. Wallace, L. Colombo, and E. M. Vogel, "Contact resistance studies of metal on HOPG and graphene stacks," *AIP Conference Proceedings*, vol. 1173, pp. 324–327, 2009.
- [40] K. Nagashio, T. Nishimura, K. Kita, and A. Toriumi, "Systematic investigation of the intrinsic channel properties and contact resistance of monolayer and multilayer graphene field-effect transistor," *Japanese Journal of Applied Physics*, vol. 49, no. 5 PART 1, p. 0513041–0513046, 2010.
- [41] Y. Sui and J. Appenzeller, "Screening and interlayer coupling in multilayer graphene field-effect transistors," *Nano Letters*, vol. 9, no. 8, pp. 2973–2977, 2009.
- [42] K. Nagashio and A. Toriumi, "Density-of-states limited contact resistance in graphene field-effect transistors," *Japanese Journal of Applied Physics*, vol. 50, no. 7 PART 1, 2011.
- [43] C. Gong, G. Lee, B. Shan, E. M. Vogel, R. M. Wallace, and K. Cho, "First-principles study of metal-graphene interfaces," *Journal of Applied Physics*, vol. 108, no. 12, 2010.
- [44] P. A. Khomyakov, G. Giovannetti, P. C. Rusu, G. Brocks, J. Van Den Brink, and P. J. Kelly, "First-principles study of the interaction and charge transfer between graphene and metals," *Physical Review B - Condensed Matter and Materials Physics*, vol. 79, no. 19, pp. 1–12, 2009.
- [45] T. Mueller, F. Xia, M. Freitag, J. Tsang, and P. Avouris, "Role of contacts in graphene transistors: A scanning photocurrent study," *Physical Review B - Condensed Matter and Materials Physics*, vol. 79, no. 24, pp. 1–6, 2009.
- [46] M. García-Mota, D. J. Oroya, E. Artacho, X. Cartoixa, and J. J. Palacios, "Integration of graphene into nanoelectronic devices: Insights from atomistic simulations," *Advanced Materials - TechConnect Briefs 2016*, vol. 1, pp. 53–56, 2016.
- [47] W. Liu, J. Wei, X. Sun, and H. Yu, "A study on graphene-metal contact," *Crystals*, vol. 3, no. 1, pp. 257–274, 2013.
- [48] K. Nagashio, T. Yamashita, J. Fujita, T. Nishimura, K. Kita, and A. Toriumi, "Impacts of graphene/ SiO_2 interaction on FET mobility and Raman spectra in mechanically exfoliated graphene films," *Technical Digest - International Electron Devices Meeting, IEDM*, pp. 564–567, 2010.
- [49] T. Cusati, G. Fiori, A. Gahoi, V. Passi, M. C. Lemme, A. Fortunelli, and G. Iannaccone, "Electrical properties of graphene-metal contacts," *Scientific Reports*, vol. 7, no. 1, pp. 1–11, 2017.
- [50] K. T. Chan, J. B. Neaton, and M. L. Cohen, "First-principles study of metal adatom adsorption on graphene," *Physical Review B - Condensed Matter and Materials Physics*, vol. 77, no. 23, pp. 1–12, 2008.
- [51] S. Wang, D. Mao, A. Muhammad, S. Peng, D. Zhang, J. Shi, and Z. Jin, "Characterization of the quality of metal-graphene contact with contact end resistance measurement," *Applied Physics A: Materials Science and Processing*, vol. 122, no. 7, 2016.
- [52] J. W. Suk, W. H. Lee, J. Lee, H. Chou, R. D. Piner, Y. Hao, D. Akinwande, and R. S. Ruoff, "Enhancement of the electrical properties of graphene grown by chemical vapor deposition via controlling the effects of polymer residue," *Nano Letters*, vol. 13, no. 4, pp. 1462–1467, 2013.
- [53] M. S. Choi, S. H. Lee, and W. J. Yoo, "Plasma treatments to improve metal contacts in graphene field effect transistor," *Journal of Applied Physics*, vol. 110, no. 7, 2011.
- [54] W. Li, Y. Liang, D. Yu, L. Peng, K. P. Pernstich, T. Shen, A. R. Hight Walker, G. Cheng, C. A. Hacker, C. A. Richter, Q. Li, D. J. Gundlach, and X. Liang, "Ultraviolet/ozone treatment to reduce metal-graphene contact resistance," *Applied Physics Letters*, vol. 102, no. 18, 2013.
- [55] W. Li, C. A. Hacker, G. Cheng, Y. Liang, B. Tian, A. R. Hight Walker, C. A. Richter, D. J. Gundlach, X. Liang, and L. Peng, "Highly reproducible and reliable metal/graphene contact by ultraviolet-ozone treatment," *Journal of Applied Physics*, vol. 115, no. 11, 2014.

- [56] C. Gong, H. C. Floresca, D. Hinojos, S. McDonnell, X. Qin, Y. Hao, S. Jandhyala, G. Mordi, J. Kim, L. Colombo, R. S. Ruoff, M. J. Kim, K. Cho, R. M. Wallace, and Y. J. Chabal, "Rapid selective etching of PMMA residues from transferred graphene by carbon dioxide," *Journal of Physical Chemistry C*, vol. 117, no. 44, pp. 23000–23008, 2013.
- [57] Y. Jia, X. Gong, P. Peng, Z. Wang, Z. Tian, L. Ren, Y. Fu, and H. Zhang, "Toward High Carrier Mobility and Low Contact Resistance: Laser Cleaning of PMMA Residues on Graphene Surfaces," *Nano-Micro Letters*, vol. 8, no. 4, pp. 336–346, 2016.
- [58] S. Gahng, C. H. Ra, Y. J. Cho, J. A. Kim, T. Kim, and W. J. Yoo, "Reduction of metal contact resistance of graphene devices via CO₂ cluster cleaning," *Applied Physics Letters*, vol. 104, no. 22, 2014.
- [59] W. S. Leong, H. Gong, and J. T. Thong, "Low-contact-resistance graphene devices with nickel-etched-graphene contacts," *ACS Nano*, vol. 8, no. 1, pp. 994–1001, 2014.
- [60] X. Ji, Y. Wang, and Z. Yu, "First-principle investigation of Ti wetting layer influence on metal-graphene contact," *International Conference on Simulation of Semiconductor Processes and Devices, SISPAD*, pp. 392–395, 2013.
- [61] S. Z. Yu, Y. Song, J. R. Dong, Y. R. Sun, Y. M. Zhao, and Y. He, "Low specific contact resistivity to graphene achieved by AuGe/Ni/Au and annealing process," *Chinese Physics B*, vol. 25, no. 11, 2016.
- [62] H. Ramamoorthy and R. Somphonsane, "In-situ current annealing of graphene-metal contacts," *Journal of Physics: Conference Series*, vol. 1144, no. 1, 2018.
- [63] Y. Zhang and X. P. Qu, "Improved contact resistivity and enhanced mobility of metal-graphene FET by inserting ultra-thin MoO_x layer at source/drain region," *AIP Advances*, vol. 9, no. 5, 2019.
- [64] F. Xia, V. Perebeinos, Y. M. Lin, Y. Wu, and P. Avouris, "The origins and limits of metal-graphene junction resistance," *Nature Nanotechnology*, vol. 6, no. 3, pp. 179–184, 2011.
- [65] A. Nath, M. Currie, A. K. Boyd, V. D. Wheeler, A. D. Koehler, M. J. Tadjer, Z. R. Robinson, K. Sridhara, S. C. Hernandez, J. A. Wollmershauser, J. T. Robinson, R. L. Myers-Ward, M. V. Rao, and D. K. Gaskill, "In search of quantum-limited contact resistance: Understanding the intrinsic and extrinsic effects on the graphene-metal interface," *2D Materials*, vol. 3, no. 2, pp. 1–13, 2016.
- [66] B. Kretz, C. S. Pedersen, D. Stradi, M. Brandbyge, and A. Garcia-Lekue, "Atomistic Insight into the Formation of Metal-Graphene One-Dimensional Contacts," *Physical Review Applied*, vol. 10, no. 2, p. 1, 2018.
- [67] M. Konig, G. Ruhl, A. Gahoi, S. Wittmann, T. Preis, J. M. Batke, I. Costina, and M. C. Lemme, "Accurate Graphene-Metal Junction Characterization," *IEEE Journal of the Electron Devices Society*, vol. 7, no. c, pp. 227–238, 2019.
- [68] A. Meersha, H. B. Variar, K. Bhardwaj, A. Mishra, S. Raghavan, N. Bhat, and M. Shrivastava, "Record low metal - (CVD) graphene contact resistance using atomic orbital overlap engineering," *Technical Digest - International Electron Devices Meeting, IEDM*, no. Cvd, pp. 5.3.1–5.3.4, 2017.
- [69] C. Yang, Z. Wang, Y. Jia, P. Peng, X. Gong, L. Ren, and Y. Fu, "Contact resistance between graphene and metal," *China Semiconductor Technology International Conference 2016, CSTIC 2016*, pp. 1–3, 2016.
- [70] D. W. Yue, C. H. Ra, X. C. Liu, D. Y. Lee, and W. J. Yoo, "Edge contacts of graphene formed by using a controlled plasma treatment," *Nanoscale*, vol. 7, no. 2, pp. 825–831, 2015.
- [71] K. Keramatnejad, Y. S. Zhou, D. W. Li, H. R. Golgir, X. Huang, Q. M. Zhou, J. F. Song, S. Ducharme, and Y. F. Lu, "Laser-Assisted Nanowelding of Graphene to Metals: An Optical Approach toward Ultralow Contact Resistance," *Advanced Materials Interfaces*, vol. 4, no. 15, pp. 1–7, 2017.
- [72] J. T. Smith, A. D. Franklin, D. B. Farmer, and C. D. Dimitrakopoulos, "Reducing contact resistance in graphene devices through contact area patterning," *ACS Nano*, vol. 7, no. 4, pp. 3661–3667, 2013.
- [73] H. Y. Park, W. S. Jung, D. H. Kang, J. Jeon, G. Yoo, Y. Park, J. Lee, Y. H. Jang, J. Lee, S. Park, H. Y. Yu, B. Shin, S. Lee, and J. H. Park, "Extremely Low Contact Resistance on Graphene through n-Type Doping and Edge Contact Design," *Advanced Materials*, vol. 28, no. 5, pp. 864–870, 2016.

- [74] R. Wang, J. Wang, H. Gong, Z. Luo, D. Zhan, Z. Shen, and J. T. Thong, "Cobalt-mediated crystallographic etching of graphite from defects," *Small*, vol. 8, no. 16, pp. 2515–2523, 2012.
- [75] S. Min Song, T. Yong Kim, O. Jae Sul, W. Cheol Shin, and B. Jin Cho, "Improvement of graphene-metal contact resistance by introducing edge contacts at graphene under metal," *Applied Physics Letters*, vol. 104, no. 18, pp. 2012–2015, 2014.
- [76] V. Passi, A. Gahoi, J. Ruhkopf, S. Kataria, F. Vaurette, E. Pallecchi, H. Happy, and M. C. Lemme, "Contact resistance Study of 'edge-contacted' metal-graphene interfaces," *European Solid-State Device Research Conference*, vol. 2016-Octob, pp. 236–239, 2016.
- [77] V. Passi, A. Gahoi, E. G. Marin, T. Cusati, A. Fortunelli, G. Iannaccone, G. Fiori, and M. C. Lemme, "Ultralow Specific Contact Resistivity in Metal–Graphene Junctions via Contact Engineering," *Advanced Materials Interfaces*, vol. 6, no. 1, pp. 1–8, 2019.



Murray, R. 2023. Laser-induced graphene-like carbon for volatile organic compound sensing. PhD Thesis, University College Cork.

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BIBLIOGRAPHY

- [1] L. A. Wallace, E. Pellizzari, B. Leaderer, H. Zelon, and L. Sheldon, "Emissions of volatile organic compounds from building materials and consumer products," *Atmospheric Environment* (1967), vol. 21, p. 385–393, Jan 1987.
- [2] G. Wieslander, D. Norbäck, E. Björnsson, C. Janson, and G. Boman, "Asthma and the indoor environment: the significance of emission of formaldehyde and volatile organic compounds from newly painted indoor surfaces," *International archives of occupational and environmental health*, vol. 69, p. 115–124, Dec 1997.
- [3] S. Batterman, C. Jia, and G. Hatzivasilis, "Migration of volatile organic compounds from attached garages to residences: A major exposure source," *Environmental Research*, vol. 104, p. 224–240, Jun 2007.
- [4] A. L. CLOBES, G. P. ANANTH, A. L. HOOD, J. A. SCHROEDER, and K. A. LEE, "Human activities as sources of volatile organic compounds in residential environments," *Annals of the New York Academy of Sciences*, vol. 641, p. 79–86, Apr 1992.
- [5] G. Wieslander, D. Norbäck, E. Björnsson, C. Janson, and G. Boman, "Asthma and the indoor environment: The significance of emission of formaldehyde and volatile organic compounds from newly painted indoor surfaces," *International Archives of Occupational and Environmental Health*, vol. 69, p. 115–124, Dec 1996.
- [6] Q. He, Y. Yan, H. Li, Y. Zhang, L. Chen, and Y. Wang, "Characteristics and reactivity of volatile organic compounds from non-coal emission sources in china," *Atmospheric Environment*, vol. 115, p. 153–162, Aug 2015.
- [7] Q. Lin, Z. Gao, W. Zhu, J. Chen, and T. An, "Underestimated contribution of fugitive emission to vocs in pharmaceutical industry based on pollution characteristics, odorous activity and health risk assessment," *Journal of Environmental Sciences (China)*, vol. 126, p. 722–733, Apr 2022.
- [8] L. Zhang, J. Wang, X. Hu, J. Zhou, M. Zhao, J. Zhang, Y. Bo, Y. Huang, and Y. Zhang, "Vocs and pm concentrations in underground parking garages of the commercial center and high-rise residential buildings," *Air Quality, Atmosphere and Health*, vol. 14, p. 1117–1131, Jul 2021.
- [9] U. Schlink, M. Rehwagen, M. Damm, M. Richter, M. Borte, and O. Herbarth, "Seasonal cycle of indoor-vocs: Comparison of apartments and cities," *Atmospheric Environment*, vol. 38, no. 8, p. 1181–1190, 2004.
- [10] D. of Criteria Documentation, Standards, N. I. for Occupational Safety, and H. (), "Occupational exposure to methyl alcohol," *Criteria for a Recommended Standard*, 1976.
- [11] NIOSH, "Occupational health guideline for methyl alcohol," tech. rep., 1978.
- [12] N. R. Council, "Interim acute exposure guideline levels (aeglss) for methanol," Tech. Rep. 50, 2008.
- [13] J. E. Cometto-Muñiz and W. S. Cain, "Thresholds for odor and nasal pungency," *Physiology and Behavior*, vol. 48, no. 5, pp. 719–725, 1990.
- [14] G. A. Blengini, C. E. Latunussa, U. Eynard, C. Torres de Matos, D. Wittmer, K. Georgitzikis, C. Pavel, S. Carrara, L. Mancini, M. Unguru, D. Blagoeva, F. Mathieux, and D. Pennington, *Study on the EU's list of Critical Raw Materials (2020) Final Report*. 2020.
- [15] Z. Wang, A. Ali Haidry, L. Xie, A. Zavabeti, Z. Li, W. Yin, R. Lontio Fomekong, and B. Saruhan, "Acetone sensing applications of ag modified tio2 porous nanoparticles synthesized via facile hydrothermal method," *Applied Surface Science*, vol. 533, no. July, p. 147383, 2020.
- [16] J. Bai and B. Zhou, "Titanium dioxide nanomaterials for sensor applications," *Chemical Reviews*, vol. 114, no. 19, p. 10131–10176, 2014.
- [17] T. Seiyama, K. Fujiishi, M. Nagatani, and A. Kato, "A new detector for gaseous components using zinc oxide thin films," *The Journal of the Society of Chemical Industry, Japan*, vol. 66, no. 5, p. 652–655, 1963.
- [18] P. J. Shaver, "Activated tungsten oxide gas detectors," *Applied Physics Letters*, vol. 11, no. 8, p. 255–257, 1967.

- [19] T. Seiyama, A. Kato, K. Fujiishi, and M. Nagatani, "A new detector for gaseous components using semiconductive thin films," *Analytical Chemistry*, vol. 34, no. 11, p. 1502–1503, 1962.
- [20] N. Yamazoe, J. Fuchigami, M. Kishikawa, and T. Seiyama, "Interactions of tin oxide surface with O_2 , H_2O and H_2 ," *Surface Science*, vol. 86, no. C, p. 335–344, 1979.
- [21] P. T. Moseley and D. E. Williams, "A selective ammonia sensor," *Sensors and Actuators: B. Chemical*, vol. 1, no. 1–6, pp. 113–115, 1990.
- [22] S. J. Kim, I. S. Hwang, J. K. Choi, Y. C. Kang, and J. H. Lee, "Enhanced C_2H_5OH sensing characteristics of nano-porous SnO_2 hollow spheres prepared by sucrose-mediated hydrothermal reaction," *Sensors and Actuators B: Chemical*, vol. 155, no. 2, p. 512–518, 2011.
- [23] J. W. Yoon, J. K. Choi, and J. H. Lee, "Design of a highly sensitive and selective C_2H_5OH sensor using p-type Co_3O_4 nanofibers," *Sensors and Actuators, B: Chemical*, vol. 161, no. 1, p. 570–577, 2012.
- [24] M. Hübner, C. E. Simion, A. Tomescu-Stănoiu, S. Pokhrel, N. Bârsan, and U. Weimar, "Influence of humidity on CO sensing with p-type Co_3O_4 thick film gas sensors," *Sensors and Actuators, B: Chemical*, vol. 153, no. 2, p. 347–353, 2011.
- [25] S. Pokhrel, C. E. Simion, V. Quemener, N. Bârsan, and U. Weimar, "Investigations of conduction mechanism in Cr_2O_3 gas sensing thick films by ac impedance spectroscopy and work function changes measurements," *Sensors and Actuators, B: Chemical*, vol. 133, no. 1, p. 78–83, 2008.
- [26] C. Wang, J. Liu, Q. Yang, P. Sun, Y. Gao, F. Liu, J. Zheng, and G. Lu, "Ultrasensitive and low detection limit of acetone gas sensor based on w-doped NiO hierarchical nanostructure," *Sensors and Actuators, B: Chemical*, vol. 220, p. 59–67, 2015.
- [27] X. Yang, H. Fu, L. Zhang, X. An, S. Xiong, X. Jiang, and A. Yu, "Enhanced gas sensing performance based on the fabrication of polycrystalline $Ag@TiO_2$ core-shell nanowires," *Sensors and Actuators, B: Chemical*, vol. 286, p. 483–492, 2019.
- [28] X. H. Yang, H. T. Fu, K. Wong, X. C. Jiang, and A. B. Yu, "Experimental and theoretical studies of $V_2O_5@TiO_2$ core-shell hybrid composites with high gas sensing performance towards ammonia," *Nanotechnology*, vol. 24, no. 41, p. 103–115, 2013.
- [29] X. Xing, N. Chen, Y. Yang, R. Zhao, Z. Wang, Z. Wang, T. Zou, and Y. Wang, "Pt-functionalized nanoporous TiO_2 nanoparticles with enhanced gas sensing performances toward acetone," *Physica Status Solidi (A) Applications and Materials Science*, vol. 215, Jul 2018.
- [30] P. K. Dutta, A. Ginwalla, B. Hogg, B. R. Patton, B. Chwieroth, Z. Liang, P. Gouma, M. Mills, and S. Akbar, "Interaction of carbon monoxide with anatase surfaces at high temperatures: Optimization of a carbon monoxide sensor," *Journal of Physical Chemistry B*, vol. 103, no. 21, pp. 4412–4422, 1999.
- [31] C. Imawan, F. Solzbacher, H. Steffes, and E. Obermeier, "Gas-sensing characteristics of modified- MoO_3 thin films using Ti -overlayers for NH_3 gas sensors," *Sensors and Actuators, B: Chemical*, vol. 64, no. 1–3, p. 193–197, 2000.
- [32] C. Wang, X. Cheng, X. Zhou, P. Sun, X. Hu, K. Shimanoe, G. Lu, and N. Yamazoe, "Hierarchical $\alpha-Fe_2O_3/NiO$ composites with a hollow structure for a gas sensor," *ACS Applied Materials and Interfaces*, vol. 6, no. 15, p. 12031–12037, 2014.
- [33] X. Li, J. Liu, H. Guo, X. Zhou, C. Wang, P. Sun, X. Hu, and G. Lu, " $Au@In_2O_3$ core-shell composites: a metal-semiconductor heterostructure for gas sensing applications," *RSC Advances*, vol. 5, p. 545–551, Dec 2014.
- [34] M. Kugishima, K. Shimanoe, and N. Yamazoe, " C_2H_4O sensing properties for thick film sensor using La_2O_3 -modified SnO_2 ," *Sensors and Actuators, B: Chemical*, vol. 118, no. 1–2, p. 171–176, 2006.
- [35] N. Barsan, C. Simion, T. Heine, S. Pokhrel, and U. Weimar, "Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors," *Journal of Electroceramics*, vol. 25, no. 1, p. 11–19, 2010.
- [36] J. W. Yoon, H. J. Kim, I. D. Kim, and J. H. Lee, "Electronic sensitization of the response to C_2H_5OH of p-type NiO nanofibers by Fe doping," *Nanotechnology*, vol. 24, no. 44, 2013.

- [37] N. Barsan and U. Weimar, "Conduction model of metal oxide gas sensors," *Journal of Electroceramics*, vol. 7, no. 3, p. 143–167, 2001.
- [38] Z. W. Pan, Z. R. Dai, and Z. L. Wang, "Nanobelts of semiconducting oxides," *Science*, vol. 291, no. 5510, p. 1947–1949, 2001.
- [39] M. Law, H. Kind, B. Messer, F. Kim, and P. Yang, "Photochemical sensing of no 2 with sno 2 nanoribbon nanosensors at room temperature," *Angew. Chem. Int. Ed*, vol. 41, no. 13, 2002.
- [40] E. Comini, G. Faglia, and G. Sberveglieri, "Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts," *Appl. Phys. Lett*, vol. 81, p. 1869, 2002.
- [41] S. J. Kim, I. S. Hwang, C. W. Na, I. D. Kim, Y. C. Kang, and J. H. Lee, "Ultrasensitive and selective c2h5oh sensors using rh-loaded in2o3 hollow spheres," *Journal of Materials Chemistry*, vol. 21, no. 46, p. 18560–18567, 2011.
- [42] F. Gyger, M. H€ , C. Feldmann, N. Barsan, and U. Weimar, "Nanoscale sno 2 hollow spheres and their application as a gas-sensing material," *Chem. Mater*, vol. 22, p. 4821, 2010.
- [43] Z. Zhong, Y. Yin, B. Gates, and Y. Xia, "Preparation of mesoscale hollow spheres of tio2 and sno2 by templating against crystalline arrays of polystyrene beads," *Advanced Materials*, vol. 12, p. 206–209, 2000.
- [44] J. H. Lee, "Gas sensors using hierarchical and hollow oxide nanostructures: Overview," *Sensors and Actuators B: Chemical*, vol. 140, no. 1, p. 319–336, 2009.
- [45] A. Kolmakov and M. Moskovits, "Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures," *Annu. Rev. Mater. Res*, vol. 34, p. 151–80, 2004.
- [46] P. T. Moseley, "Solid state gas sensors," *Measurement Science and Technology*, vol. 8, no. 3, p. 223–237, 1997.
- [47] N. Yamazoe and K. Shimano, "New perspectives of gas sensor technology," *Sensors and Actuators, B: Chemical*, vol. 138, p. 100–107, Apr 2009.
- [48] N. Barsan, C. Simion, T. Heine, S. Pokhrel, and U. Weimar, "Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors," *Journal of Electroceramics*, vol. 25, no. 1, p. 11–19, 2010.
- [49] G. C. Bond, L. R. Molloy, and M. J. Fuller, "Oxidation of carbon monoxide over palladium-tin(IV) oxide catalysts: An example of spillover catalysis," *Journal of the Chemical Society, Chemical Communications*, no. 19, pp. 796–797, 1975.
- [50] K. Großmann, S. Wicker, U. Weimar, and N. Barsan, "Impact of pt additives on the surface reactions between sno2, water vapour, co and h2; an operando investigation," *Phys. Chem. Chem. Phys*, vol. 15, p. 19151–19158, 2013.
- [51] T. Seiyama and S. Kagawa, "Study on a detector for gaseous components using semiconductive thin films," *Analytical Chemistry*, vol. 38, no. 8, p. 1069–1073, 1966.
- [52] N. Murata, T. Suzuki, M. Kobayashi, F. Togoh, and K. Asakura, "Characterisation of pt-doped sno2 catalyst for a high-performance micro gas sensor," *Phys. Chem. Chem. Phys*, vol. 15, p. 17938, 2013.
- [53] T. Suzuki, S. Soma, and T. Nagase, "Methane Sensor for Cordless Utility Gas Alarms," *Fuji Electric Review*, vol. 84, no. 4, pp. 278–282, 2012.
- [54] N. Yamazoe, Y. Kurokawa, and T. Seiyama, "Effects of additives on semiconductor gas sensors," *Sensors and Actuators*, vol. 4, no. C, p. 283–289, 1983.
- [55] D. Degler, H. W. Pereira De Carvalho, K. Kvashnina, J. D. Grunwaldt, U. Weimar, and N. Barsan, "Structure and chemistry of surface-doped Pt:SnO2 gas sensing materials," *RSC Advances*, vol. 6, no. 34, pp. 28149–28155, 2016.
- [56] D. Degler, S. Rank, S. Müller, H. W. Pereira De Carvalho, J. D. Grunwaldt, U. Weimar, and N. Barsan, "Gold-Loaded Tin Dioxide Gas Sensing Materials: Mechanistic Insights and the Role of Gold Dispersion," *ACS Sensors*, vol. 1, no. 11, pp. 1322–1329, 2016.

- [57] D. Degler, S. A. Müller, D. E. Doronkin, D. Wang, J. D. Grunwaldt, U. Weimar, and N. Barsan, "Platinum loaded tin dioxide: A model system for unravelling the interplay between heterogeneous catalysis and gas sensing," *Journal of Materials Chemistry A*, vol. 6, no. 5, pp. 2034–2046, 2018.
- [58] M. Hübner, N. Bârsan, and U. Weimar, "Influences of al, pd and pt additives on the conduction mechanism as well as the surface and bulk properties of sno2 based polycrystalline thick film gas sensors," *Sensors and Actuators B: Chemical*, vol. 171–172, p. 172–180, 2012.
- [59] M. Epifani, S. Kaciulis, A. Mezzi, T. Zhang, J. Arbiol, P. Siciliano, A. Landström, I. Concina, A. Moumen, E. Comini, and C. Xiangfeng, "Rhodium as efficient additive for boosting acetone sensing by tio2 nanocrystals. beyond the classical view of noble metal additives," *Sensors and Actuators, B: Chemical*, vol. 319, no. May, 2020.
- [60] H. Fu, X. Yang, X. An, W. Fan, X. Jiang, and A. Yu, "Experimental and theoretical studies of v2o5@tio2 core-shell hybrid composites with high gas sensing performance towards ammonia," *Sensors and Actuators, B: Chemical*, vol. 252, p. 103–115, 2017.
- [61] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, and J. M. Tour, "Laser-induced porous graphene films from commercial polymers," *Nature Communications*, vol. 5, p. 5714, Dec 2014.
- [62] R. Ye, Y. Chyan, J. Zhang, Y. Li, X. Han, C. Kittrell, and J. M. Tour, "Laser-induced graphene formation on wood," *Advanced Materials*, vol. 29, p. 1702211, Oct 2017.
- [63] R. Ye, D. K. James, and J. M. Tour, "Laser-induced graphene," *Accounts of Chemical Research*, vol. 51, no. 7, p. 1609–1620, 2018.
- [64] A. Imbrogno, J. Islam, C. Santillo, R. Castaldo, L. Sygellou, C. Larrigy, R. Murray, E. Vaughan, M. K. Hoque, A. J. Quinn, and D. Iacopino, "Laser-induced graphene supercapacitors by direct laser writing of cork natural substrates," *ACS Applied Electronic Materials*, vol. 4, no. 4, p. 1541–1551, 2022.
- [65] C. Larrigy, M. Burke, A. Imbrogno, E. Vaughan, C. Santillo, M. Lavorgna, L. Sygellou, G. Paterakis, C. Galiotis, D. Iacopino, and A. J. Quinn, "Porous 3d graphene from sustainable materials: Laser graphitization of chitosan," *Advanced Materials Technologies*, vol. 2201228, 2022.
- [66] M. Burke, C. Larrigy, E. Vaughan, G. Paterakis, L. Sygellou, A. J. Quinn, G. Herzog, C. Galiotis, and D. Iacopino, "Fabrication and electrochemical properties of three-dimensional (3d) porous graphitic and graphenelike electrodes obtained by low-cost direct laser writing methods," *ACS Omega*, vol. 5, no. 3, p. 1540–1548, 2020.
- [67] Y. Dong, S. C. Rismiller, and J. Lin, "Molecular dynamic simulation of layered graphene clusters formation from polyimides under extreme conditions," *Carbon*, vol. 104, pp. 47–55, 2016.
- [68] R. Murray, M. Burke, D. Iacopino, and A. J. Quinn, "Design of experiments and optimization of laser-induced graphene," *ACS Omega*, vol. 6, p. 16736–16743, Jul 2021.
- [69] D. Iacopino, E. Vaughan, C. Larrigy, M. Burke, L. Sygellou, A. J. Quinn, and C. Galiotis, "Visible laser scribing fabrication of porous graphitic carbon electrodes: Morphologies, electrochemical properties, and applications as disposable sensor platforms," *ACS Applied Electronic Materials*, vol. 2, p. 3279–3288, Oct 2020.
- [70] G. Paterakis, E. Vaughan, D. R. Gawade, R. Murray, G. Gorgolis, S. Matsalis, G. Anagnostopoulos, J. L. Buckley, B. O'Flynn, A. J. Quinn, D. Iacopino, and C. Galiotis, "Highly sensitive and ultra-responsive humidity sensors based on graphene oxide active layers and high surface area laser-induced graphene electrodes," *Nanomaterials*, vol. 12, no. 15, 2022.
- [71] M. G. Stanford, K. Yang, Y. Chyan, C. Kittrell, and J. M. Tour, "Laser-induced graphene for flexible and embeddable gas sensors," *ACS Nano*, vol. 13, no. 3, p. 3474–3482, 2019.
- [72] R. Murray, O. O'Neill, E. Vaughan, D. Iacopino, A. Blake, C. Lyons, D. O'Connell, J. O'Brien, and A. J. Quinn, "Direct-write formation of integrated bottom contacts to laser-induced graphene-like carbon," *Nanotechnology*, vol. 33, no. 40, 2022.

- [73] S. Jaśkaniec, S. R. Kavanagh, J. Coelho, S. Ryan, C. Hobbs, A. Walsh, D. O. Scanlon, and V. Nicolosi, "Solvent engineered synthesis of layered snO₂ for high-performance anodes," *npj 2D Materials and Applications* 2021 5:1, vol. 5, p. 1–9, Mar 2021.
- [74] L. Yang, G. Zheng, Y. Cao, C. Meng, Y. Li, H. Ji, X. Chen, G. Niu, J. Yan, Y. Xue, and H. Cheng, "Moisture-resistant, stretchable NO_x gas sensors based on laser-induced graphene for environmental monitoring and breath analysis," *Microsystems and Nanoengineering*, vol. 8, no. 1, 2022.
- [75] A. Vázquez-López, D. Maestre, J. Ramírez-Castellanos, and A. Cremades, "In situ local oxidation of snO₂ induced by laser irradiation: A stability study," *Nanomaterials*, vol. 11, no. 4, 2021.
- [76] K. J. Saji, Y. P. Venkata Subbaiah, K. Tian, and A. Tiwari, "P-type snO₂ thin films and snO₂/ZnO heterostructures for all-oxide electronic and optoelectronic device applications," *Thin Solid Films*, vol. 605, p. 193–201, Apr 2016.
- [77] Z. Ouyang, W. Wang, M. Dai, B. Zhang, J. Gong, M. Li, L. Qin, and H. Sun, "Research progress of p-type oxide thin-film transistors," *Materials* 2022, Vol. 15, Page 4781, vol. 15, p. 4781, Jul 2022.
- [78] K. J. Saji and A. P. R. Mary, "Tin oxide based p and n-type thin film transistors developed by rf sputtering," *ECS Journal of Solid State Science and Technology*, vol. 4, p. Q101–Q104, Jul 2015.
- [79] M. Hübner, D. Koziej, J. D. Grunwaldt, U. Weimar, and N. Barsan, "Au clusters related spill-over sensitization mechanism in SnO₂-based gas sensors identified by operando HERFD-XAS, work function changes, DC resistance and catalytic conversion studies," *Physical Chemistry Chemical Physics*, vol. 14, no. 38, pp. 13249–13254, 2012.
- [80] T. Itoh, Y. Koyama, W. Shin, T. Akamatsu, A. Tsuruta, Y. Masuda, and K. Uchiyama, "Selective detection of target volatile organic compounds in contaminated air using sensor array with machine learning: Aging notes and mold smells in simulated automobile interior contaminant gases," *Sensors (Switzerland)*, vol. 20, no. 9, 2020.
- [81] N. X. Thai, M. Tonezzer, L. Masera, H. Nguyen, N. v. Duy, and N. D. Hoa, "Multi gas sensors using one nanomaterial, temperature gradient, and machine learning algorithms for discrimination of gases and their concentration," *Analytica Chimica Acta*, vol. 1124, p. 85–93, 2020.
- [82] Z. Zhu, C. T. Kao, and R. J. Wu, "A highly sensitive ethanol sensor based on Ag@TiO₂ nanoparticles at room temperature," *Applied Surface Science*, vol. 320, p. 348–355, 2014.
- [83] S. M. Majhi, A. Mirzaei, H. W. Kim, S. S. Kim, and T. W. Kim, "Recent advances in energy-saving chemiresistive gas sensors: A review," *Nano Energy*, vol. 79, Jan 2021.

5.1 Conclusions

This work sought to develop a LIG-based VOC sensor as a route to produce resource-efficient sensors for use under ambient conditions. However, LIG has a complex formation process, which had limited its development as a material platform. Therefore it was necessary to develop a system-agnostic, design-of-experiment optimisation route for LIG production; which could be rapidly redeployed for alternative material substrates, dopants, laser system or wavelength.

Further, LIG devices lacked a reproducible, reliable contacting method, instead relying on direct mechanical or expensive, cross-contaminating silver paint contacts. This hampered the practical implementation of LIG-based device into real systems. This required the development of novel, all-laser, electrical back-contact methods to allow for the practical implementation of future devices. With sufficient stability of the LIG material-platform, and a viable integration route, a low-resource, room temperature VOC sensor was developed.

Insight and inspiration were drawn from adjacent studies on graphene and metal oxide materials. Given the diversity of these applications and the breadth of investigations, a series of synopses are included in the Introduction (Chapter 1) and in the appendices of this work. The combination of these foundational works in the context of the investigation of LIG should provide a firm starting point for future investigations.

Chapter 2 demonstrated the successful, resource-efficient, use of iterative design of experiment methods in the determination of optima and factor interactions in complex, novel material systems, such as LIG. This approach facilitated the development of both low-sheet resistance and high-throughput LIG material on a hobbyist laser-system. The method-focused optimisation, allowed for the transfer to the higher specification laser system used in the remainder of this work, and can be generalised to any other LIG production route. The employment of design of experiment methods in this work demonstrate not only its efficiency as an optimization strategy but also its use as a rigorous, resource-efficient investigation tool.

Chapter 3 focused on the development of aq direct-write laser method to enable rapid fabrication of LIG structures with integrated low-resistance contact plugs to buried metal layers.

We demonstrated contact resistances as low as $\sim 30\ \Omega$ for Ni layers ($\sim 50\ \Omega$ for Au) using 4-plugs in parallel, comparable with LIG sheet resistance. Further resistance reduction (~ 5 -fold) is envisaged through increased contact areal density and material optimisation. The back-contact method demonstrated provides a stable, reproducible contact sufficient for sensing applications, as demonstrated with proof of concept electrochemical sensors. Further optimisation would be required for energy storage applications. These results highlight the potential for efficient integration of LIG-based, high-surface area sensor electrodes with buried metal layers.

Chapter 4 reports a resource-efficient LIG-based VOC sensor, functionalised with SnO nanoflowers for head-space detection, under mimicked ambient conditions. These sensors integrate the optimised LIG platform with a low mass-loading of separately prepared functionalisation material. This yielded a VOC sensor with sensitivity to methanol headspace vapor ($\sim 5\%$ at 150 ppm, $\sim 35\%$ at 4100 ppm), rapid response times ($t_{90}=35\text{ s}$ @ 150 ppm methanol, 5s recovery) and stability > 21 days, competitive with existing resource-intensive chemiresistive MOX sensors in a versatile, low-cost custom chamber.

Resource efficiency was the central theme underpinning this thesis. It influenced not only the experimental design, as is evident through the use of, iterative, design of experiment methods, but also the conscious material choices. This manifests in the use of non-critical materials for NP functionalisation of the final sensors and also in the back-contact design, minimising additional process steps and resources.

5.2 Contributions to Knowledge

Table 5.1, summarises the challenges in the development VOC sensors from LIG identified in Sections 2.1, 3.1 and 4.1. The advancements are reiterated in Table 5.2. The challenges and their advances can be identified by their labels (e.g. Ch.2.1 and Ad.2.1.1). 31 contributions to the knowledge addressing the 12 challenges are identified. These gave rise to the two published papers and prepared manuscript included in this thesis. The addressed challenges had limited the greater uptake of LIG-based devices, as high-quality, low resistance LIG could only be produced on high-cost equipment, available in few labs. The generalisation of the method onto lower cost laser systems with an simple optimisation framework broke down these barriers to entry, and opened the field to more investigations.

I addressed the lack of robust contacting methods to LIG. This advancement allows for new and exciting device geometries to be investigated while ensuring good electrical access. This work focused on both Ni and Au, which are typical chemisorbing and physisorbing metals for carbon systems respectively. In the graphene literature, there is no conclusive evidence as to whether chemisorbing or physisorbing metals are preferable, therefore this work also acts as a foundation for further investigations in LIG. With the integration challenges addressed, the final experimental chapter addressed the development of a VOC sensor. This chapter proposed a novel metal oxide sensitising agent SnO, fabricated under mild conditions, and a simple dropcast-self assembly construction on previously fabricated LIG electrodes. The resulting sensor operated well at room temperature and humidity with good selectivity to alcohols vs. humidity.

Label	Challenge
Ch.1.1	High cost laser systems required
Ch.1.2	High Resistance LIG material is produced
Ch.1.3	<i>Ad-hoc</i> optimisation of complex multifactor experimental space
Ch.1.4	Limited knowledge of impact of laser parameters on LIG quality
Ch.2.1	Current contact methods for LIG are high cost, non-scalable and risk damage/contamination
Ch.2.2	Uncertain literature on best contacting metals for graphene
Ch.2.3	Commercially unavailability of polyimide on arbitrary metal films
Ch.2.4	Complex system dependence for successful LIG formation
Ch.3.1	State of the art sensors use critical raw materials and high temperature fabrication routes (400°C synthesis, 1000°C calcination)
Ch.3.2	Standard methods use high resource cost interdigitated Au electrodes
Ch.3.3	Standard sensors operate at high temperature (>350°C)
Ch.3.4	VOC gas sensing systems are typically prohibitively expensive

Table 5.1: List of challenges addressed in the Thesis.

Label	Advances
Ad.1.1	Demonstration of LIG formation on hobbyist CO ₂ laser system
Ad.1.2.1	Demonstration of contemporaneous lowest observed sheet resistance (~ 15 Ohm/sq.)
Ad.1.2.2	Development of high-throughput visual assessment criteria for LIG quality assessment
Ad.1.2.3	Demonstration of resource efficient sheet resistance estimation method
Ad.1.3.1	Development of Laser-system agnostic iterative, multifactor design of experiments optimization route for LIG
Ad.1.3.2	Demonstration of Iterative DoE optimisation for a novel CO ₂ laser system
Ad.1.3.3	Discovered high throughput-low sheet resistance formation conditions at non-intuitive laser parameters
Ad.1.4.1	First reported implementation of Eckmann et al.'s Raman analysis on LIG to interpret defect types
Ad.1.4.2	Demonstration of proof of concept, all-polymer, capacitive humidity sensors based on LIG
Ad.2.1.1	First Demonstration of a LIG-metal contact
Ad.2.1.2	Development of a robust, all-laser, back contacting method
Ad.2.2.1	First demonstration of a successful back-contacted device
Ad.2.2.2	Identification of metal-type dependency of on contact formation
Ad.2.2.3	Demonstration of contact method dependence on electrochemical properties
Ad.2.2.4	Outline of potential future scaling routes
Ad.2.3.1	Development of a double spin-coating method for the generation of controlled polyimide thickness
Ad.2.3.2	Development of lithography-free contact resistance estimation method
Ad.2.4.1	Demonstration of minimum polyimide thickness requirement for quality LIG formation
Ad.2.4.2	Establishment of viable laser conditions parameters for back-contacting
Ad.2.4.3	Observation of carbon self-encapsulation of contact region
Ad.2.4.4	Identification of contact perimeter, not areal, scaling
Ad.3.1.1	First demonstration of SnO as a VOC sensing element
Ad.3.1.2	First demonstration of room temperature VOC sensing using LIG
Ad.3.2.1	Development of LIG mediated self-assembly of SnO pseudo-wires
Ad.3.2.2	Demonstration of device stability of over 21 days
Ad.3.3.1	Successful detection of methanol (LOD: 170 ppm) below the 8hr worker safety limit (200 ppm) at room temperature
Ad.3.3.2	Demonstration of low cross-selectivity to humidity
Ad.3.3.3	Proposal of low-temperature appropriate VOC sensing mechanism
Ad.3.4.1	Development of low-cost VOC sensing system using labware, 3D printing and hobbyist electronics
Ad.3.4.2	Public distribution of 3D models via github
Ad.3.4.3	Confirmed concentrations of gas phase analytes with photoionisation detector

Table 5.2: List of advancements beyond the state of the art.

5.3 Future Work

This thesis has demonstrated advancements of the LIG fabrication platform, providing a novel route to contact LIG and successfully produce a low-resource, low-energy VOC sensor. However, there are numerous fruitful avenues for further work.

Design of Experiments and Optimization of Laser-Induced Graphene-like Carbon

The DoE work was completed with a focus on polyimide-based feedstock materials and a CO₂ laser system. However, there is increasing interest in the literature towards using biopolymers and organic feedstocks. Understandably these novel feedstocks introduce additional complexity into the fabrication of LIG. Some of these materials may require significant chemical preparation steps, different laser sources and/or multiple laser treatments, e.g. chitosan, while others may be directly usable, e.g. cork. In either case, optimisation of these feedstock materials presents a significant increase in complexity over the more mature polyimide feedstock. As such, DoE methods would facilitate rapid advancements of lower-resource cost LIG.

Direct-write Formation of Integrated Bottom Contacts to Laser-Induced Graphene-like Carbon

The direct-write formation of integrated bottom contacts was demonstrated in this work using a Si support wafer and spun-cast polyimide produced in-fab. However, as was stated in that work, the resource-intensive fabrication route and supporting wafer are not essential to its success. Rather, they were used to allow the investigation of different support methods, vary polyimide thickness and ensure reproducibility. Further investigations will focus on the development of back contacts using commercially available Al-backed polyimide in order to reduce the resource cost of this contacting method further. Al-backed films are chosen due to its low-cost, abundance and biodegradability, this would allow for the future integration of these contacting methods with biopolymer feedstocks.

Room Temperature Sensing of Volatile Organic Compounds using hybrid SnO Nanoflowers and Laser-Induced Graphene-like Carbon devices

The most exciting avenue for future work builds on the developments shown in Chapter 4. This work focused on the development of a methanol sensor using SnO nanoflowers synthesised in IPA, to achieve room temperature sensors suitable for worker safety monitoring. These devices, like all pristine semiconducting MOX, have limited sensitivity. However, it is expected that changing the particle morphology, by varying the synthesis solvent and reflux temperature, would yield a different cross-selectivity fingerprint, due to change in abundances, and interfaces, of different crystalline planes. Orthogonal sensor arrays of hybrid SnO-LIG could thus be fabricated via dropcasting, avoiding the high-temperature or high-energy functionalisation processes typically required.

The resulting orthogonal sensing array would allow for the development of a principal component regression machine learning layer. This approach takes multiple sensors with similar, but distinct, cross-selectivities and trains a model on known gas mixtures. The end goal is a collaborative sensor system that is more than the sum of its parts, that can both identify the analyte, by the response fingerprint across the array, and subsequently correctly determine its concentration.

Mechanistic insight to the specific analyte interactions of different morphologies, due to their crystalline plane combinations, should be sought in parallel via molecular dynamics simulations. The resulting work would thus present an in-depth view of the sensor response behaviour, allow greater interpretation of the sensor array output and assist in the design of future particle morphologies.

The final sensor array, should then be interfaced with a wireless communication enabled portable electronics measurement circuit, as a proof of concept demonstrator. This would emphasise the benefits of such a low power system to demonstrated. In particular, it would not require heating for operation, unlike typical chemiresistive VOC sensors. The end result would be a robust, interdisciplinary investigation of a low-power sensor array primed for the internet of things with clear applicability for worker safety monitoring at industry relevant VOC concentrations.

5.4 Impact

This work has garnered great interest in the research community, with two first author papers in high impact factor journals, three presentations in international conferences, Table 5.3. These works have had a significant impact on the field resulting in the adoption of their methods and optimisation routes, as well as interest from industry groups manifesting in the form of an invited poster to an Industry conference, Table 5.4.

My first paper has received 15 citations, since publication in June of 2021. The citing papers referencing not only the low resistance values achieved, but also its demonstration of the highly complex optimisation space and the iterative optimisation route proposed. My second paper, although more recent, only being published in July of 2022, has already recognised by both the Tyndall Postgraduate Publication of the Year and the University College Cork, College of Science, Engineering and Food Science Post graduate Publication of the Year Award in 2022.

The developments have also facilitated and supported other works directly, leading to several co-authored works ranging from energy storage and biopolymer LIG feedstocks to Surface Enhanced Raman Spectroscopy and Electrochemistry, Table 5.3.

Beyond these research outcomes, I have supervised three summer students and have been involved in the supervision of new PhD students in designing their scheme of work, data analysis and upskilling to our current methods. The developed work has been a key pillar of our education and public engagement, with age appropriate introductions to electricity, sensors and additive manufacture being developed for group ranging from primary school to undergraduate audiences.

Publication	Citations	First Author	Year	Link
Design of Experiments and Optimization of Laser-Induced Graphene-like Carbon	15	Yes	2021	Link
Direct-write Formation of Integrated Bottom Contacts to Laser-Induced Graphene-like Carbon	1	Yes	2022	Link
Room Temperature Sensing of Volatile Organic Compounds using hybrid SnO Nanoflowers and Laser-Induced Graphene-like Carbon devices	n/a	Yes	Pending	n/a
Laser-Induced Graphene Supercapacitors by Direct Laser Writing of Cork Natural Substrates	15	No	2022	Link
Highly Sensitive and Ultra-Responsive Humidity Sensors Based on Graphene Oxide Active layers and High Surface Area Laser-Induced Graphene Electrodes	7	No	2022	Link
Silver Nanoparticles-Laser Induced Graphene (Ag NPs-LIG) Hybrid electrodes for electrochemical-surface enhanced Raman Spectroscopy (EC-SERS) Detection	0	No	2023	Link
Laser Induced Graphene (LIG) Biosensors Derived from Chitosan: Towards Sustainable and Green Electronics	0	No	Preprint	Link

Table 5.3: List of Publications.

Conference	Format	Title
EMRS Spring 2022	Presentation	Optimising rapid laser fabrication of 3D porous graphene sensors using Design of Experiments methods
EMRS Fall 2022	Presentation	Direct-write Formation of Integrated Bottom Contacts to Laser-Induced Graphene-like Carbon
EMRS Spring 2023	Presentation	Room Temperature Sensing of VOC compounds using hybrid SnO Nanoflower and LIG devices
Confirm Conference 2022	Presentation	Laser Induced Graphene for Volatile Organic Compound Sensing
Nanoseries 2023	Invited Poster	Room Temperature Sensing of Volatile Organic Compounds using Hybrid SnO Nanoflowers and Laser-Induced Graphene Devices
Analog Industry Day 2022	Poster	Laser-fabricated Graphene from Polyimide: Integration with Buried Metal Contacts and Impedance Sensing of Volatile Organic Compounds

Table 5.4: List of Conferences.

Appendices

A.1 Particle Miniaturisation in p-type MOX

The main discussion focused on the dominant semiconductor type demonstrated in literature for VOC sensing, n-type. However, p-type semiconductor MOX sensors have been shown to be less sensitive to particle size than n-type [1]. The p-type conduction is already primarily mediated through the hole accumulation layer at the skin surface. Therefore, there is no equivalent of the sensitivity enhancement seen for n-type when the inter-core connectivity is eliminated as this was already the minority conduction path. In p-type conduction, the high-resistance region (bulk core) is not part of the essential conduction path, unlike n-types high-resistance skin which must be traversed to pass between grains. As this inner core is not well modulated by gas exposure, nor is it part of the critical conduction path, the magnitudes of response changes are limited in p-type sensors and their further optimisation by particle size scaling [2].

In addition to p-type sensing not gaining the same miniaturisation benefits as n-type, an in-depth analysis by *Hübner et al.* found that, with everything else being held equal, the proportional sensitivity of a p-type sensor would be the square root of that of the n-type equivalent [3]. This is exacerbated by the series contribution of contact resistance to the nanoparticle array. While this contribution is typically unmodified by the chemical environment it adds a non-trivial series resistance to the measurement circuit [4]. This is in series to the sensor load, so it can dominate the total resistance in low-resistance systems. n-type sensors don't experience this limitation, as the numerous highly resistive neck/junctions, arranged in series, dominate the total resistance, overshadowing the contact resistance contribution.

However, as p-type particles decrease their resistance during transduction, they don't demonstrate the same proportional response as their n-type counterparts. While increasing electrode gap-width can be used to mitigate the contact resistance contribution, other strategies are required for enhancing p-type sensors, such as n-doping to increase their baseline resistance through pair-recombination, while retaining p-type nature, to ensure they dominate the resistance contributions. However, this is a non-selective optimisation route [5], increasing the proportional response of any influence.

A.2 Particle Decoration

Generic models of noble particle decorations on semiconductor MOX have not yet been established, but considerable numbers of works have been demonstrated with combinations of decorating particles and supporting semiconductor MOX. The majority of mechanistic investigations have been empirical in nature, and largely focus on the dominant, SnO_2 ; consequentially, the discussion here will similarly focus on SnO_2 . Investigation of the oxidation state of typical decorating metals, on SnO_2 , show that Au tends to exist as a metallic particle in surface clusters, while Pt and Pd exist as oxides, even in strongly reducing environments [6–9]. The Pt and Pd decorating particles are therefore not expected to act as a spill-over catalyst for reception, but instead, contribute to transduction, through Fermi-level control.

A comparative study of Pt and Pd decorated SnO_2 in low oxygen environments show differing reaction schemes, whereby Pd- SnO_2 sensors respond to CO, with recovery in low oxygen environments like undecorated SnO_2 sensors, while Pt-decorated SnO_2 cannot recover until oxygen is reintroduced. This is explained by the Pt-decorated SnO_2 reaction yielding CO_2 , from the oxidation of CO via depletion of lattice oxygen. In the absence of oxygen the reduced SnO_2 , cannot be re-oxidised, resulting in the Pt-decorated SnO_2 not recovering the absence of atmospheric oxygen. This points towards different interaction schemes being opened up by the introduction of Pt on SnO_2 [7].

Further investigations of the effect of humidity on Pt and Pd decorated SnO_2 detection of CO, which is typically deleterious for CO detection on SnO_2 . Pt decoration reduced the negative impact that humidity had on CO detection, relative to undecorated SnO_2 [10]. Mechanistic studies, using deuterated water, clarify the enhancement. Without Pt decoration CO and H_2O compete for the same adsorbed oxygen species, while Pt decorations introduce a Pt-O interaction site that favours the CO interaction over that of the H_2O [11]. This mitigates the humidity-associated deactivation of the sensing mechanism and is a key demonstration of how metal decoration can open alternative, chemically specific reaction routes.

Pd-decoration of SnO_2 , in contrast, shows a different mechanism than Pt-decoration for CO detection. Humidity exposure enhances the detection of CO, on Pd-decorated SnO_2 , instead the typical attenuation seen for undecorated SnO_2 . The homolytic dissociation of water on Pd

particles which yields additional hydroxyl groups, centred at Sn sites, is responsible for this enhancement. The enhanced surface hydroxyl concentration facilitates the oxidation of CO to CO₂ [12]. Pd-decoration enhances sensor response by inhibiting the undesired water interaction, enhancing the concentration of reactants for the desired pathway, while Pt-decoration provided an alternative reaction route, without mitigating the water reaction.

Already, the broad scope of surface decoration resulting from different particle decorations on the same MOX is evident. Candidate sensors are often fabricated without mechanistic insight and investigated for sensing enhancement, however, less commonly MOX and decorations are chosen on the basis of known reactivities, i.e. Pt catalysis of hydrocarbon breakdown [13]. The previously outlined enhancement routes combine enhancement with a degree of specificity, due to the underlying chemical interactions at the surface. However, doping can also enhance sensor response, without altering the specificity. This is ascribed to the pre-depletion of charge carriers prior to surface interactions, which enhances the proportional influence of surface adsorbates [14]. The unspecific enhancement produced is due to its impact on the transduction and not the sensing mechanism. This can be combined with subsequent decoration, where the doping alters the baseline resistance, enhancing the proportional response of the decorating materials [15].

An overview of the complexity of the effects of noble metals on a single MOX, SnO₂ has been demonstrated here, however, it is increasingly popular in the literature to dope one MOX with another. While this opens additional sensitisation routes, it adds significant complexity to the mechanism. Considering an example case of the co-decoration of CuO and La₂O₃ on TiO₂ [16]. CuO facilitates the spill-over of adsorbed CO onto the TiO₂ surface, but produced poor thermal stability of TiO₂. The La₂O₃ slowed the structural change and enhanced the oxygen depletion, allowing for more strongly bound carbonate species. Their co-deposition enhanced both the oxygen site adsorption and the spill-over of CO enhancing the reaction rate, and thus the response.

In addition to the spill-over and Fermi-level pinning arguments discussed so far, the combination of MOXs can also introduce p-n junctions. However, the underlying mechanism is often not discussed [17]. Therefore this brief summary will focus on systems that have been investigated mechanistically, e.g., Fe₂O₃ (n-type) decoration of NiO (p-type), whereby the sensing enhance-

ment is ascribed to the heterojunction. The higher Fermi level of Fe_2O_3 results in electrons transferring into the NiO and the transfer of holes back into the Fe_2O_3 ; producing a depletion layer. This effectively pre-depletes the carrier concentration, increasing the proportional effect that adsorbed oxygen species [18], similar to doping effects discussed earlier, but with the added consideration of decoration materials carrying out secondary processes as already outlined.

A.3 Particle Morphology

Chemiresistive VOC sensors were initially demonstrated as thin films [19,20], but at present the focus of the literature is on functionalised-nanoparticle MOX VOC sensors. They are typically comprised of calcinated or sintered thick films of interconnected NPs (e.g., unmodified NP, decorated/doped NP, core-shell structures, Core-Shell/Hollow Shell) or high aspect ratio structures (e.g., ribbons, nanowires, nanorods, etc.). Each have their own advantages in terms of sensitivity, selectivity, stability, reproducibility and ease of fabrication and will be discussed in turn.

The general morphological arguments and scaling laws have already been discussed during the p-/n-type discussion, section 1.4.3. This discussion has largely assumed spherical nanoparticles or thin film systems, and other morphologies will be considered relative to this understanding. For MOX sensors NPs behave the same as the bulk, but with the notable change that their small dimensionality enhances sensing response by ensuring the depletion layer width is competitive with particle size for a considerable enhancement in sensor response. In addition to this, they have a high surface-area/volume ratio, enhancing the number of possible interaction sites/unit volume. This optimisation route is typical of other catalytic optimisations seen for nanoparticles.

Nanowires, and adjacent morphologies (nanoribbons, nanotubes, nanorods), have been demonstrated using various MOX materials (ZnO , TiO_2 , In_2O_3 , CdO , GaO) [21], and processing conditions ranging from evaporation and crystal growth to electrospinning [22–24]. They can be considered as an intermediate between the behaviours of thin films and spherical nanoparticle morphologies. Unlike bulk thin films, they have a dimensionally controlled current path for free charge carriers, and unlike spherical nanoparticles, they lack the periodic grain/neck effects previously seen. In contrast, the nanowires high aspect ratio continuous material allows for good

baseline conductivities [25, 26].

The high surface area/volume ratio results in the effective modulation of depletion/accumulation layers, this combined with the controlled conduction path further amplifies the influence of any perturbation along the nanowire length. At small nanowire cross-sections, typically smaller than the depletion layer thickness effective modulation can be caused even by a single adsorption event. Given the confined condition path, the resulting perturbation would then impact all charge carriers that must traverse that region [26] and allow for large gain due to multiple interactions along the same wire. However, this amplification can also give rise to noise and stability challenges [22, 27–29].

Electrospun nanowires, beyond providing a facile fabrication route, compared to lithographically defined ribbons, can also form numerous parallel pathways simultaneously as fibril bundles. The presence of multiple parallel pathways, mitigates the influence of noise, originating from single wire paths [30]. As with other semiconductor MOX-based sensing systems, nanowires can also be decorated with other materials to enhance their sensing performance, e.g., Pd decorated SnO₂ ribbons for O₂ and H₂ detection [31].

Core-shell decoration morphologies for nanoparticles allow for enhancements distinct from those of surface decorations and can be applied in addition to either spherical or high aspect ratio morphologies. For instance, the Ag@SnO₂ core-shell structures have enhanced sensing performance relative to SnO₂ or Ag decorations on SnO₂. This is ascribed to the conductive silver core reducing the system resistance, by providing a low resistance central core, ensuring efficient charge exchange and interconnectivity of the SnO₂ shell, and the surface SnO₂ being more easily reduced relative to the bulk SnO₂ [32].

MOX@MOX core-shell structures have also been demonstrated, e.g., ZnO@SnO₂ core-shell nanowires. Both materials are n-type semiconductors but there was still a charge transfer and association depletion layer formation at their interface, reinforcing the typical electron depletion layer that arises from oxygen adsorption, resulting in complete deletion. Conduction through n-type particle networks has already been shown to be dominated by surface interface conduction and interfaces between particles. Therefore, for n-type MOX shells, regardless of the core, the dominant conduction contribution is governed by the shell [33]. However, the core can still

enhance adsorption and other catalytic processes.

The particle miniaturisation arguments discussed earlier, in terms of p-/n-type semiconductors (section 1.4.3) can be taken to a further extreme in the form of hollow shell nanoparticles. These particles are typically spherical and comprised of a thin shell of MOX material encapsulating a central void. This produces a structure that is essentially all surface, however, unlike solid particles of equivalent size, hollow particles also allow for the diffusion of reactants inside their structure, where they can interact, effectively doubling their surface area [25, 34]. Further, the absence of a bulk core, restricts conduction through only the shell, which is easily modulated by surface interactions. These hollow shell nanoparticles have been demonstrated in numerous materials, e.g., SnO_2 , In_2O_3 , TiO_2 and C [35–37], using sacrificial scaffolds [38, 39], self-assembly [40] and emulsion templated growth [41, 42] methods.

Hollow nanoparticles can also take advantage of the catalysing effects of decorating particles. This allows for their response behaviour to be enhanced, not only by the increased surface area effects granted by the permeable thin surface of their hollow structure but also by the spill-over effects or Fermi-level pinning influences already outlined [43]. However, these influences are enhanced by the small thickness of the shell, meaning the depletion layer thickness is large relative to the particle size (thickness) ensuring a large response. Further, the permeability of the thin shell ensures good diffusion of reactants, which could otherwise be limited by solid particle interfaces.

More exotic morphologies are possible, such as hollow-shell-core nanoparticle systems. These comprise of a hollow nanoparticle shell encapsulating another solid nanoparticle. These systems have been employed in multiple applications including site-specific drug transport, energy storage and gas sensing applications [44–46]. It is possible to use catalytic cores within MOX encapsulating shells to further enhance their sensing properties, e.g., an Au core in a SnO_2 shell which enhance reception and spill over of oxygen species [44]. The Au cores, in this morphology have good separation from each other, preventing aggregation and ensuring maximum surface area for oxygen adsorption, as with typical nanoparticle decorating particles [47].

Despite the many alternative morphologies demonstrated since thin-films, there is a renewed

interest in using doped thin films for lower-power operations, due to their low thermal mass. Which requires less energy to be expended to achieve the necessary working temperature, and opens up alternative perturbative heating schemes for periodic measurements, reducing the time spent at elevated temperature, instead of continuous heating of large mass thick films [48,49].

B- CONTACT RESISTANCE

Contact resistance is a key barrier preventing the reliable and reproducible implementation of graphene and graphene-like material based devices. This has limited graphene-based technologies from laboratory investigations to industrial environments. The focus of the majority of the literature has been towards GFET applications, using pristine graphene. However, the same contact resistance mitigations are essential in applications monitoring the change of a resistance element, e.g., chemiresistive sensing, where a high or variable contact resistance diminishes the proportional response observed and limits device-to-device reproducibility.

Therefore this discussion will utilise the well established literature for pristine graphene and GFET applications as a foundation towards the discussion of LIG contacting strategies, given that it is known to consist of numerous interconnected few-layer graphene sheetlets.

B.1 Pristine Graphene

In traditional semiconductor device fabrication, contact resistance is well understood, with origins including differences in band structures, p-n junction formation and injection barriers. However, due to its one-dimensional structure and zero-volume, graphene deviates from the behaviour of both metals and semi-conductors. Graphene has a linear electronic dispersion, consequentially it has a low DOS at its Dirac point. Due to its low carrier concentration, lack of bulk material to pin the Fermi level and highly available surface area graphene is highly sensitive to its environment. Unlike normal metals, which would attenuate external perturbations as $1/x$, graphene instead only modulates them as $1/\sqrt{x}$, due to its low carrier density. This results in longer range effects. Multi-layer graphene systems instead display the $1/x$, dependence, due to its larger carrier concentration. Although, the initial contact resistance values can be larger due to the modified band structure. This enhanced screening is present from even 2-3 layers [50–52]. Exacerbating the influence of its small DOS, the high surface area of graphene ensures pronounce extrinsic dependences. Further the small DOS and zero band gap results in even a small charge transfer producing a dramatic change in the Fermi energy of the graphene [53]. This is distinct from higher DOS metals, attenuating small charge transfers without modifying their Fermi-level.

Accounting for these influences, for graphene-based devices to challenge current Si-based CMOS devices they should have contact resistances below $100 \Omega\mu m$ [54].

One key component in minimising the contact resistance is the choice of metal used. Two broad classes of metals have been determined relative to the graphene sheets; **physisorbed** and **chemisorbed**. The physisorbed metal transfers charge carriers into the graphene but does not result in a rehybridisation of the molecular orbitals, preserving the electronic band structure of the graphene sheet. While, chemisorbed metals do result in a change in the hybridisation, $sp^2 \rightarrow sp^3$, altering the electronic structure and opening a band gap in the (formerly) semi-metal graphene. Further distinctions between the physisorbed and chemisorbed metals are observed in their conduction mechanisms. Chemisorbed contacts directly inject charge into the sheet, while physisorbed metals experience a barrier that must be overcome. Physisorbed metals are predicted to have higher contact resistances. However, the chemical bonding required by the chemisorption does modify the underlying graphene, potentially resulting in a deviation from the ideal properties of the graphene being pursued. Therefore, the in-plane modifications, on top of the absolute contact resistance, need to be considered to determine the better contact.

Physisorbing metals have weaker adsorption energies (0.03-0.05eV/carbon) and larger bond distances ($> 3\text{\AA}$) than chemisorbed metals (0.09-0.4eV/carbon and $< 2.5\text{\AA}$). The down shifting of graphene energy levels relative to the metal due to Pauli exclusion results in the doping of the contacted graphene [55]. The influence of the barrier on contact resistance in physisorbing metals is significant. Investigations using initial Ti adhesion layers (forming a monolayer of chemisorbed material) with further physisorbed metals layers produced a reduced contact resistance for all sampled physisorbing metals. The chemisorbed Ti modified the graphene, decreasing the Fermi velocity but to a lesser degree than would be seen for multilayers/full contacts. The choice of metal(s) is therefore clearly a significant parameter in order to minimise both the contact resistance but also to preserve other desirable characteristics of the graphene being contacted [56]. Collated in Table B.1. are the metals that have been determined to be physisorbed/chemisorbed and, where known, the doping it causes in the graphene sheet.

As has been previously described the choice of metal, to a large degree, determines the contact resistance. These metals also have preferential sites, that influence how they interact with the

Table B.1: Collated Metal types indicating, where known, graphene adsorption type and doping interaction.

Metal	Sorption	Doping	source
Al	Physi	N	[57]
Ag	Physi	N	[57]
Cu	Physi	N	[57]
Au	Physi	P	[57]
Pt	Physi	P	[57]
Cd	Physi		[55]
In	Physi		[55]
Ni	Chemi		[55]
Co	Chemi		[55]
Ru	Chemi		[55]
Pd	Chemi		[55]
Ti	Chemi		[55]

sheet. As shown in Fig. B.1, there are three distinct sites the top site, hollow and bridge. These sites offer differing access to the hybridised and un-hybridised orbitals of the graphene sheet. The hollow site is a region of low electron density but has a high coordination to the carbon atoms, allowing energetically favourable donation of electrons by the metal. The top and bridge sites instead provide more direct access to the molecularly orbitals of the graphene. Therefore, physisorbing metals prefer the hollow site, while chemisorbing metals the bridge/top sites [58]. The introduction of contaminants/gases that have preferential sites would disproportionately affect the contact of metals that would also utilise that site. Similarly, the presence of structural defects in the graphene sheet could influence interactions with contact metals. Most simulations do not make provisions for grain boundaries, Stone-Wales defects or account for the effects of adsorbed-non-reactive gases (e.g. CO₂, O₂ and N₂). *Garcia-Mota et al.* investigated this, in terms of Pd contacted graphene. It was noted that the gases resulted in charge doping of the graphene but without significant Fermi-level change. Further, the extent of molecular physisorption was not seen to be affected by the presence of the intrinsic structural defects [59]. It is promising to see that these neglected components do not have a significant effect, however, that they have any influence does suggest that known doping gases such as water vapour should be considered more closely in simulated works. Especially as asymmetry has been observed with applied potential, suggesting the formation of pn-junctions.

Other environmental influences should also be considered, for example the supporting

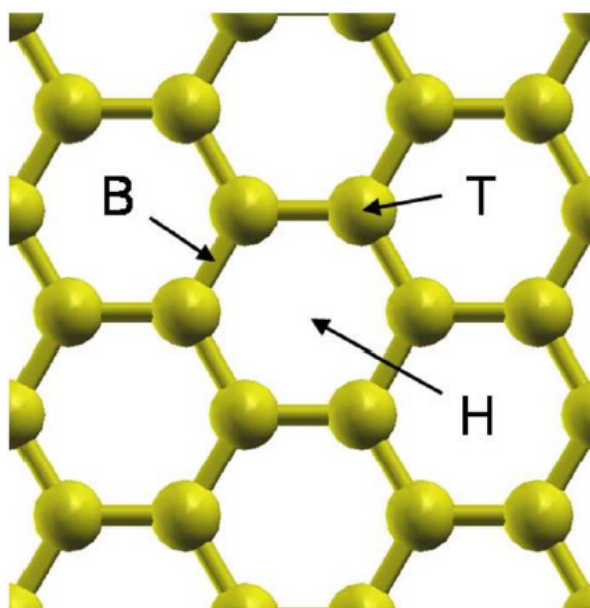


Figure B.1: Adsorption sites on graphene, B (bridge), T (top) and H (hollow) sites are noted, reproduced from *Chan et al.* 2008 [58].

substrate. Silicon dioxide, an insulator, is often used as a non-interacting surface that can be easily and quickly formed on Si wafers, as such it is a favoured substrate for transferring CVD grown graphene for further process steps. Normally the surface termination of the oxide surface is an insignificant influence on further layers, however the environmental sensitivity of graphene results in a dependence. The -OH terminated surface results in p-doping for the graphene while the -O termination n-dopes [46, 60]. This would alter the doping profile and hence any pn-junctions that are formed. This source of variability isn't widely considered in the literature and could contribute to the broad range of contact resistance values seen for different metals.

In either form of contact there is an associated charge redistribution, although this is less clearly defined for chemisorption, in the case of physisorption this can be understood in terms of p/n-doping. Depending on the work function of the contact metal the charge redistribution can result in a net p/n doping depending on the electron withdrawal/donation from/to the graphene sheet. This change over point is 5.4 eV, up-shifted from the intrinsic graphene work function (4.5 eV), due to the formation of an interface dipole. The dipole forms as a result of the overlap of metal electron density and the graphene molecular orbitals (Pauli exclusion). This dipole induced work function dependence was noted to decrease with distance as expected from its suggested orbital overlap influence. While for chemisorbed metals they would not experience the dipole, due to

the rehybridization. However, in plane charge redistribution, due to modified graphitic band structures, would effectively dope the graphene [57]. The charge doping of graphene sheets has been verified by photocurrent spectroscopy. Indicating that built-in electric fields are generated due to charge redistribution as a result of metal contacting the graphene. This doping was seen to extend into material up to 2 nm beyond the contacted region [61].

These correspond to the observed asymmetry of electrons and hole conduction with opposite potentials, as differing resistances would be observed in the formation of a p-p, n-n or p-n junctions. It is already known from other works that water vapour adsorbing onto graphene sheets results in a small p-doping. The localised n-doping of the graphene sheet by a contact metal can thus result in pn-junction formation. As noted previously, their formation has been observed from the device's asymmetry with applied potential. As a positive potential would result in a pn-junction forming, while a negative potential would form a pp-junction, a lower resistance conformation [53]. Further works have investigated the use of the gate potential to alter charge doping in a GFETs configuration modifying the device asymmetry, supporting the pn-junction determination [62].

These physically observed sources of resistance dependences correspond with those predicted by the quantum mechanical model of *Xia et al.* [63]. Whereby the conduction is considered in two main parts; the injection from metal to graphene and then the transfer from the doped graphene into the channel region. This work indicates that the contact resistance depends on the DOS under the metal in the channel (which is modified by the metal), the carrier tunnelling probability (determined by the barrier, work functions) and the tunnelling probability (controlled by the doping and pn-junction). This set out three components that could be targeted to reduce the contact resistance. This work was expanded on, with focus on the behaviours of different metals in the graphene-metal contact. It was noted that the contact resistivity depended on the equilibrium. Extreme cases of Ni and Al for the smallest/largest distance and contact resistivity respectively were observed. However, concerns regarding the potential influence on lateral current conduction mechanisms do need to be further considered in the case of chemisorbed metals as previously noted [64].

The determined correlation between contact resistance and metal-graphene equilibrium

distance provided a grounding for later works. Notably simulations of graphene sheet edge terminations typical of those produced through oxidative etch methods, used to define channel dimensions, were investigated. The attraction experienced, towards these edges, by contacting metals depended on the termination nature. Maximal attraction was felt towards clean, uncontaminated edges. For Ni, oxygen termination resulted in a decreased attraction, and a more extreme decrease with fluorine termination (approx. 2 orders of magnitude). The decrease in attraction corresponds to an increase in equilibrium separation. Although not all metals considered acted in the same way as Ni. Cr showed relative independence from the edge termination, and Ti resulted in a reorganisation of the surface removing contaminants away from the graphene edge to allow for a better contact. The presence of the defective material would result in an increase contact resistance due to its separation from the graphene sheet. This is exacerbated for the monovalent F only being able to form one bond further increasing the separation of the graphene from the metal. The chosen metals sensitivity to separation is also critical for producing consistent contacts. It was suggested that the overlooking of this source of variability is a partial cause of the variability seen in contact resistance values in the literature [65].

The literature so far has been inconclusive on the optimal metal for contacting graphene. Large variability is seen between groups, both in the absolute values for the contact and in their relative ordering. Considering the archetypal metal studied for each class of contact (physisorption/chemisorption), Au and Ni. Depending on the work and its methodologies the optimal metal may be either Au or Ni. However, some initial works have been carried out to illustrate why such variability has been observed. Likely sources of variability have been identified including metal deposition processes, process step conditions, environmental interactions, metal work function, graphene layer number and resist residues/contaminants. As has already been noted, a significant component of this is the different distance dependences seen for physisorbing metals vs. chemisorbing metals. Chemisorbed metals have shorter range interactions; as such, the presence of contaminants or other perturbations that would increase separation are amplified relative to the influence they would have on longer ranged physisorbed metals. Though physisorbed metals are more site specific, showing sensitivity to the configuration of the graphene surface [66]. Similarly, if the graphene sheet is wrinkled the equilibrium distance

of the metal to the surface is increased negatively effecting the chemisorbed contact resistance more significantly than that of physisorbed contacts [67]. Meaningful comparisons of different design methodologies have not yet been carried out, but this appears to be another likely source of variability in contact resistance leading to the ambiguity seen in the literature.

The mechanism used to form the contacts needs to be considered. For example, in the case of depositing Ti metal contacts. A distinction was observed when deposition was achieved through ebeam compared with that formed using sputtering. The sputtered contact had a higher contact resistance associated with damage to the graphene sheet, due to the higher momenta of the deposited particles. It is also possible that the smaller grain size from the ebeam deposition would result in shorted contact distances [46], decreasing the contact resistance. Similarly, other mechanism dependent processes need to be considered. For example, wet vs dry processing of CVD grown graphene contacted by Al display different contact resistances. The wet processed Al, dipped in DI water, has a larger contact resistance corresponding to the formation of an interfacial oxide between the graphene and metal contact which acts as a barrier to charge injection. This unintended contaminant formation is a likely source for variability seen in literature. Such influences should be considered in any contaminant removal procedures [68].

The Quantum Mechanical (QM) consideration coupled with the distance dependence provides a good general framework for the consideration of contact resistance in a graphene-metal contact. However, it is critical to expand beyond these core considerations to account for alternative contacting geometries. The initial QM methodology assumed that it was a top-contacted graphene structure and as such defined potential regions for optimisation. It would be easy to assume that these would stand for more recent methods such as edge-contacted graphene or holey-graphene. This sets out a potential pitfall in optimisation procedures whereby primary sources of resistance in one geometry are negligible in another. Simulations of both embedded and edge contacted Ni-Graphene contacts indicated that in the case of the embedded contact that a three order of magnitude reduction in the contact resistivity in a top-contacted device would result in only a 40% reduction in the total contact resistance. Experimentally the contact resistivity has been seen to be reduced to $\leq 1\%$ of its initial value through carbide formation when annealed. So, unless contact resistivity is determined to be the dominant factor, then its optimisation should not be the

focus of any optimisation process as it has a limited impact on the total contact resistance and has known minimisation methods. It was seen that unlike in the case of the embedded structure, the edge contact structure only had a one-step electron transfer process, deviating from the quantum mechanical model previously discussed. In the edge contacting the charge can transfer directly into the sheet, as such, the contributions to the overall contact resistance and their scaling is distinct from that of a top contact and should be optimised separately [69]. This is considered later in terms of the Landauer-Buttiker quantum mechanical model, Equ. B.2.

As previously noted, thermal annealing is a known method used to heal damage caused during fabrication, form better contacts by decreasing grain size or to remove contaminants. In graphene it has been explored for each of these roles. Surprisingly, in the previously discussed Ti deposition comparing ebeam and sputtered Ti contacts to graphene, a decrease in graphene quality was observed post annealing, signalled by a shifted in the graphene G peak in its Raman spectrum. [70]. Other works, however, have observed, the expected decrease in the contact resistivity due to annealing in a hydrogen environment. This was proposed to be due to the removal of PMMA resist from the uncontacted graphene, metal grain size becoming more uniform - providing better contact- or the dissolution of carbon into the metal allowing for the formation of numerous end-contacted regions [71]. The proposal of the metal grain size modification is like the arguments by *Liu et al.* about why the E-beam deposited Ti has a lower contact resistance as well as the sample metal contact separation dependence. This is a complex component of the contact resistance that requires further consideration, especially due to the potential damage that could occur to the graphene.

The total resistance of a TLM can be divided into two main components, the channel resistance and the contact resistance, whereby $R_T(L) = R_{Ch}(L) + 2R_C$. The contact resistance is the measure of the resistance of the device due to injecting charge from the leads into the device through a given contact region. As this is not part of a future device's role, it is considered a parasitic component that should be minimised. In traditional semiconductor devices, planar metallic interfaces are used, taking advantage of the isotropic nature of the substrate. Additionally, doping steps are normally taken to ensure good Fermi-level and band alignments between the semiconductor and the metal. If the resulting Fermi-level is in the band gap a Schottky barrier

forms, if it is below the valence band/above the conduction band an Ohmic contact forms. The height of any barrier formed depends on the metal work function and electron affinity of the semiconductor. Consequently, for high barrier interactions tunnelling must occur for charge injection increasing contact resistance [72]. The Schottky barrier makes it more difficult for charge to be injected into the channel and as such increases the contact resistance.

Traditional considerations of current flow would suggest a homogenous distribution of charge across a planar interface between two materials. Whereby contact resistance would decrease as a function of the area of the contact (in line with $R = \rho L/A$). However, if the resistivity of the contacted layer is large relative to the contact metal, or if the transition resistance in the contact region is large (due to energy band structures at the interface) then a deviation from the expected contact can occur [73]. Current crowding is the term given to describe the arising phenomena. Current, instead of uniformly entering the contacted material, instead travels the maximum distance in the contacting metal before entering it. Consequently, there is a larger current density at the extreme most portion of the contacting metal. This occurs as the metal dominant pathway is the path of least resistance. This occurs in metal graphene contacts despite the graphene's high conductivity due to its low density of states, making it challenging to inject charge [53]. The current crowding changes the scaling of the contact resistance with its geometry. Below a given length, transfer length (L_T), the device scales as expected (areally), when $L > L_T$ the contact no longer depends on the length of the contact. Instead the contact resistance scales linearly with the width of the contact. Modelling of TLM contacts in graphene suggest a further deviation from the transfer length seen in the more general current crowding situation, with further factors determining the true L_T although that suggested initially is the limiting case. It was further seen that that the current crowding results in Joule heating [74].

To account for the theoretical complications arising from current crowding/spreading alternative contacting methods beyond the traditional TLM have been suggested such as circular TLM analogues [75]. Those contacts would account for current spread/crowding but require numerical benchmarking and transformation which has not found significant use, despite it not requiring edge patterning of graphene. However, some of the assumptions of the TLM have been challenged further. These include its assumption of each contact being equivalent, which would

not account for defect distributions due to the transfer process of even CVD grown graphene and other less well controlled processes. Consequently, it has been suggested that caution should be taken in its use to ensure repeatability and sufficiently large contacts should be used to account for the current crowding [76]. The defect dependence of the TLM method is also a candidate for the higher variability it is seen to produce relative to the 4-probe methods. [71]. Recently, single metallisation step processes were realised for determining graphene-metal contact resistance determination. This modified the Cross-Kelvin 4-probe method, facilitating facile determination of contact resistance, while providing greater alignment leeway [68]

Achieving low contact resistance graphene-metal interfaces is complicated by the short transfer length decreasing the active area of the contact used. Further, the presence of residues or contaminants at an interface between metals or semiconductors will increase its resistance either due to acting like a traditional resistor or due to providing an additional barrier through which charge must tunnel. It is for this reason that many cleaning steps are integrated into semiconductor manufacturing processes; every photolithography step results in residue that could damage the resulting contacts. Normally, high energy/temperature or organic molecule focused removal methods are used to clean interfaces prior to metallisation including plasma ashing or acid dips. Similarly, Rapid Thermal Annealing (RTA) is often used to ensure good contact geometries are maintained utilising the full contact area.

Graphene is not a traditional semiconductor or metal. It is a monolayer, semimetal with zero bandgap. Consequently, the way it must be handled and considered for device manufacture differs from traditional semiconductors. Due to its linear dispersion around its Dirac point it also has a low density of states, this coupled with its all surface zero volume structure makes it very sensitive to environmental influence. Further it is prone to damage from methods normally used in device manufacture and cannot be subjected to the same extremes of temperature or chemical environment. This presents challenges in how it can be handled but also in the methods needed to ensure high quality, low contact resistance metallisation processes can be achieved.

Considering the biggest distinction first, the low density of states, introduces additional factors that can normally be neglected, namely charge induced doping from metal contacts, substrate interactions and environmental doping. Pristine graphene often becomes p-doped due

to interactions with oxygen moieties, water molecules and other volatile organic compounds, however depending on the work function of contacting metal used, it is possible for the contacted graphene to become n- or p-doped; resulting in potential pn-junction formation, device asymmetry and increased contact resistance. This contact induced doping also results in a further split in the channel resistance as the graphene below the contacted metal will then behave differently than the un-contacted material of the channel. Thus, alternative measurement geometries such as end-contact resistance should be utilised [77].

The limitation of cleaning processes caused by the sensitivity of graphene results in unintentional knock on effects. Residues from photoresist, a core component of photolithography cannot be easily removed from graphene without causing damage. While less damaging methods are unable to fully remove the residues. Instead a compromise between the two extremes is necessary resulting in insulating residue remaining present in the interface region of metallic contacts, increasing contact resistance. These residues can also act as scattering sites and as charged dopants further diminishing the materials properties for which the graphene was selected initially. This challenge is further heightened due to the low throughput of pristine graphene methods such as SiC epitaxial growth or mechanical exfoliation. Instead, chemical vapour deposition graphene (CVD-G) is used as large surface areas can be produced rapidly.

During CVD growth of graphene, a stream of methane is incident on a copper foil which facilitates the growth of graphene. Later the graphene is covered with a PMMA handling layer and the copper foil is etched away. The graphene is then transferred to its desired substrate and the PMMA handling layer is removed. However, this removal is incomplete. The residue increases the contact resistance. Although vacuum annealing and other processes can be used to remove this residue. It is noted that its removal results in a $2\times$ increase in mobility. It is also noted that for CVD-G extrinsic scattering dominates device properties. Acetone and vacuum annealing can mostly remove the PMMA, but Raman analysis suggests its incomplete removal. Further, re-exposing the sample to PMMA would re-increase the observed p-doping; suggesting that it was its presence and not damage to the sample that cause the shift [78]. Later works that removed the residue using contact Atomic Force Microscopy (AFM) observed no change in the quality of the graphene as characterised by Raman spectroscopy. This is indicative of a

physisorbed material that does not damage or modify the underlying graphene. The non-chemical nature of the bonding limits the charge doping that can occur due to the residue and allows for a wider range of removal methodologies [79].

Residues of PMMA handling layers and photoresist, increase the contact resistance through several different processes. These include the intuitive aspect of being a layer of resistive material at the interface, however the other aspects can also influence the behaviour such as their role in increasing the metal-graphene separation dramatically increasing the resistance associated with the highly distance dependent tunnelling process. Further, the residue present is not homogenous and therefore its influence over the resulting contact is not predictable, preventing consistent device production. Its removal would not only reduce the contact resistance but also reduces the device to device variability [80]. This is key, as high contact resistance device, although not ideal can still be utilised, while unpredictable devices cannot.

The considerations outlined can be considered in a simplified quantum mechanical model as has already been suggested, in terms of metal-graphene separation distances, Landauer-Buttiker model Equ. B.2. The veracity of the use of the model has been assessed using a residue-free metallisation process on epitaxially grown graphene on SiC produces a high quality, low contaminant graphene platform for investigating metal contact behaviours. Assuming full transmission, the theoretical limit for contact resistance should be $88 \Omega\mu m$ for side contacts (top or bottom). However, unlike CVD-G, epitaxially grown graphene lacks high-energy defect sites on its surface for carbide formation resulting in a higher contact resistance as the transfer coefficient is reduced. These dangling bonds are equivalent to the edge site carbons with their higher energy sp-hybridisation, which act as a high energy site for bond formation to deposited metals as well as providing accessible molecular orbitals for charge transfer. As such increasing the number of sp-hybridised carbons present in the sheet will allow for a reduction in the contact resistance [81].

Further the controlled, intentional introduction of contaminants was conducted to investigate influences on the Ni contact. The contaminants were seen to cause higher sheet resistances suggestive of charge transfer from the graphene sheet reducing electron density. The Ni could also interact with the residue to produce insulating material preventing charge transfer. In terms

of the Landauer-Buttiker model, it is possible to capture the geometry of the contact in terms of the transfer coefficients, as a side contact $T < 0.1$, while for an edge contact $T > 0.5$. This captures the difficulty in overcoming charge barriers to injection for a side contact that are not present for a metal that can bond to a higher energy dangling bond at an edge site, formally T_{MG} tends to 0 for edge contacts as graphene is an insulator out of plane, while it tends to 1 for carbide bonds. Further T_{MG} can also be used to capture insulating influences of interfacial residues and distance dependences. Similarly, T_{CC} can be used to characterise the tunnelling barrier introduced by differing doping profiles in the contacted and channel graphene, namely if pn-junctions are present. This experimental work alongside quantum mechanical consideration highlights the main optimisation routes for graphene contacts: interface optimisation, doping profiles, contact geometry [82].

$$R_c = \frac{1}{T} \frac{h\sqrt{\pi}}{4e^2\sqrt{n}} \quad (\text{B.1})$$

$$T = \frac{T_{cc}T_{MG}}{(1 - (1 - T_{CC})(1 - T_{MG}))} \quad (\text{B.2})$$

Where T is the transmission coefficient, n is the carrier density, T_{CC} is the transmission coefficient between the contacted graphene and the channel region, T_{MG} is the transmission coefficient between the metal and contacted graphene.

Similar investigations into the influences of residue on monolayer and bi-layer graphene have been carried out, achieving contact resistance $< 100 \Omega\mu m$. This was achieved by depositing a blanket layer of Au prior to patterning, which could then be removed in undesirable regions. The analysis again compares to Landauer's quantum mechanical model $R_c = h/4e^2MT$, $M = \Delta E_f/\pi\hbar v_F$ and T is the transfer coefficient. There is a differing dependence on the doping concentration for both the mono and bilayer graphene values whereby $M \propto \sqrt{n_s}$ for monolayers and $\propto n_s$ for bilayers. So, under the assumption that T the transmission coefficient is 1 and determining n_s values it is seen that $R_c \text{ BL} < R_c \text{ ML}$ due to higher n_s . Further it can be considered that less resist means T is closer to one. Both monolayer (4.17eV) and bilayer (4.66eV) graphene have work functions less than gold (5.1eV) so become p-doped when in contact. BL graphene is intrinsically p-doped so as n_s increases, R_c decreases, while for MG which is n-type it becomes less n-type so R_c increases [83].

As has been noted one way to reduce the contact resistance is to increase T_{MG} towards one, this can be achieved in several ways, one of the most obvious is to avoid the charge injection barrier entirely through the formation of carbide bonds. However, except for edge sites it is challenging for metallisation steps to overcome the high energy C–C bonds. Non-chemical methods have been attempted to selectively (spatially) break C–C bonds through targeted laser irradiation to form higher energy defect sites localised only within the desired contact region. This avoids damage to the graphene channel while allowing for additional edge contacts to be achieved [84].

From this brief insight into the quantum mechanical aspect three main methods to ensuring low contact resistance are possible; doping of the graphene sheets to prevent pn-junction behaviour and increase mobility, increasing T_{cc} ; reduction and removal of residue, increasing the T_{MG} ; increase chemisorption bonding behaviour between metal and graphene; increasing T_{MG} . Although, these aspects are not fully independent of each other, for the sake of clarity they will be discussed separately.

B.2 Graphene Modification

The challenges associated with low density of states of graphene and the resulting limitation of charge injection can be overcome by doping the graphene. However, unlike traditional semiconductor materials which are bulk in nature, ion implantation or diffusion would cause severe damage to graphene that could not be rectified through annealing. Instead, a polymer mixture can be used to dope the graphene instead. This relies on the low DOS of graphene and sensitivity to its environment as previously outlined. Consequently, a mix of Poly(4-vinylphenol)/Poly(melamine-co-formaldehyde) (PVP/PMF) can be used to n-dope the graphene. PVP is used as a filler component in the polymer mix, while the PMF contains triazine groups which are electron rich, resulting in n-doping of the graphene. The ratio of the mixture can be controlled to tune the extent of doping. The polymer also insulates the graphene from external influence. The n-doping must first overcome the native p-doping of the graphene to achieve intrinsic behaviour prior to n-doping to begin.

After strong n-doping occurs the choice of metal used to contact the graphene is seen to be

insignificant, as the metal-charge induced doping is no longer the dominant doping contribution forming pn-junctions [85]. Alternative polymer doping approaches have also been attempted, Hexaazatriphenylene Hexacarbonitrile similarly observing doping of the graphene tuning work functions and reducing contact resistance. It was seen that by controlling the duration of the anneal that different levels of polymer doping could be achieved. As has been shown, controlled doping of graphene sheets requires careful control over the composition of materials in which it encounters. Thus, hydrophilic layers (ODST) cast onto SiO₂ wafers to prevent trap states, water or SiO₂ defects doping the graphene uncontrollably have also been investigated [86].

The control over the interaction doping of graphene can be used in other aspects such as the band gap opening in bilayer graphene. Noting that graphene becomes p-doped from environmental interactions and electron withdrawal by oxygen moieties, it is possible to control the graphene doping by coating the top surface with triazine. Allowing the base of the graphene to interact as usual results in an inhomogeneous doping profile and built-in electric field that can be used to open up the band gap to 111 meV [87]. This again highlights the significance of which interactions are permitted and which are prevented from occurring. The metal contacts themselves need to be considered carefully as the choice of metal (work function and lattice mismatch) can influence the graphene layer. It has been shown that the choice of invasive or external probes needs to be made with some care and knowledge of the doping of the channel region and the charge induced doping that will be caused by the metal. If the doping caused by the metal were to induce a doping profile different to that of the substrate a pn junction would form, acting as a barrier to charge injection. By use of external contact structures to a graphene channel it is possible to mitigate the charge induced doping. This acts as a design rule informing the nature of metals that can be used device designs [88].

B.3 Interface Cleaning

As has been already noted, the presence of interfacial residual resist in a graphene metal interface disrupts charge transfer. This resist usually originates from both PMMA handling layers during CVD-G growth or from photolithography steps. The contamination caused by the PMMA can be mitigated through use of lower concentration PMMA solutions in the handling layer which results in less residue and lower levels of p-doping [89]. It is considered as unavoidable that some degree of residue will need to be removed. The necessity to remove the residue presents challenges especially for graphene-based devices not normally experienced in semiconductor manufacture processes. As standard residue removal steps such as plasma cleaning, ashing or chemical cleans would also damage the graphene. Alternative methods and modified traditional approaches have been developed in their place. For example, UV-Ozone methods have been used to remove residues achieving contact resistances of $200\ \Omega\mu m$ without significant modification of graphene quality, demonstrated by Raman spectroscopy and the unaltered sheet resistance. The removal of residue was verified by XPS. The duration of the UV-ozone treatment could also be tuned to ensure all of the resist is removed but stopped before damage occurs to the graphene sheet [80, 90].

Other non-destructive processes include dehydrogenation of PMMA residue through a N_2 anneal followed by a flow of CO_2 used to reduce the residue, removing oxygen groups that can bond to the graphene. This both reduces its adhesion and ability to act like a charged impurity. Although little further work has been done on the removal of the surviving hydrocarbon backbone [91]. Targeted region specific approaches such as laser cleaning have been attempted to remove the residue, although it couldn't fully remove the residue due to strong adsorption effects. This was attempted using a Raman system so that real time feedback could be achieved, it observed that monolayer graphene allows for more rapid removal of residue than CVD-G due to the higher energy defect sites present. It further noted that removal of the channel residue reduced the p-doping experienced [92].

Novel cleaning methods such as CO_2 cluster cleaning have been investigated. Utilising cooled CO_2 gas passing through a narrow opening to form cooled clusters of particles. Which when incident on the residue absorb energy and cause their rapid thermal shrinkage and removal

from the graphene substrate. Cleaning efficiency can be tuned with cluster size and particle velocity. The low energy of the cooled gas clusters ensures that no damage to the graphene sheet occurs, producing graphene sheets with lower roughness than even mechanically exfoliated samples. Although it is noted that the CO₂ clusters can induce hole-type defects in the surface, which could be a potential site for edge contacting [93].

Plasma cleaning processes are popular for semiconductor devices but can cause damage to graphene if used to remove residue. Comparison of different plasmas and their influence indicate that their damage manifests as increased edge sites resulting in reduced contact resistance. This damage can disrupt the graphene's other electrical properties so should be constrained to the contact region. Plasma treatments successfully modify the phobicity of the surface beyond just removal of the residue achieving reductions in contact angles. However, increased sp³ character and presence of CH, OH and COC functional groups in addition to vacancies is observed. The damage caused to the graphene, does however make it easier for other metals with lower binding energy to adhere to the surface. H₂ plasma was the least damaging to the graphene sheet, with O₂ and Ar being more impactful due to their chemical reactivity and large mass respectively. The plasma treatments also resulted in p-doping due to hydrogenation, oxidation and increased environmental sensitivity [94].

Tying in closely with the study and effects associated with the presence of residue on graphene is the interactions and effect that metallisation would produce. The deposition of Ni and its subsequent removal, results in no change to the graphene Raman spectra. If annealed and the prior to the removal of the metal, then a D band appears in the Raman spectrum. There is an altering of both atomic arrangement and the electronic properties of the contaminated graphene. These influences initiate from the edges of the graphene sheet, as they are regions of higher energy and thus reactivity. This occurs by a dissolution-precipitation interaction. Whereby C–C bonds break as C is dissolved into Ni. The dissolved C can then be precipitated as a Ni-C bond. When the Ni is removed, the carbide bond is broken leaving dangling, edge carbons. The defect Raman peak increases. The increase in carbide formation was verified by XPS. Similar behaviour is not replicated by Au, suggesting that the choice of metal impacts on the resulting nature and interaction with the graphene [95].

A greater insight into the interaction of metal alloys is therefore relevant. Metal alloy contacting stacks were used to contact the graphene, it was observed that $\text{Au}_{0.88}/\text{Ge}_{0.12}/\text{Ni}/\text{Au}$ has a lower contact resistivity than Ti/Au and $\text{Ti}/\text{Pt}/\text{Au}$ metal contacting stacks on graphene. This is despite the known carbide formation of Ti and the physisorption of Au. Further for both the Ti and AuGe alloy contact resistance reductions were observed for rapid thermal anneals both prior to metallisation and post-metallisation. The anneal can reduce the contact resistance through one of three pathways; decrease interfacial residue, improve surface area, or enhance bonding. The latter of these pathways is suggested due to the inability for the residue to escape from the interface region once metallised and its prevention for significant surface area enhancement. Ge carbide formation also allows for direct contacting by Au to occur in addition to the 4p orbitals of Ge having a good overlap with the sp^2 orbitals of graphene further reducing contact resistance. Other alloys can be used to better contact graphene through orbital overlap optimisations [96]. Similarly, Cr/Au metal stacks with a monolayer of Cr can achieve reductions of contact resistance from $400 \rightarrow 200 \Omega\mu\text{m}$, again due to the removal of the charge injection barrier experience by a physisorbed Au contact [97]. More complex systems have also been considered such as MoOx layers acting as hole injection layers due to their high work function. The heavily p-doped the graphene which increases the Fermi-level but also the DOS due to the linear dispersion [98].

Not only the choice of contacting metal is important, as it is also necessary to ensure that the material used is in the expected form needed, both in terms of phase and contacting geometry. The influences of processes such as rapid thermal annealing, often used for ensuring ideal metallic contacts, is considered, however in the case of graphene-based devices it can result in unintended damage to the channel region as well as defects in the contact region. Despite this, it has been demonstrated to form more stable and consistent contacts. For example, prior to RTA, contact resistance values were seen to be large and skewed while after a RTA step they decreased in value in addition to adopting a Gaussian distribution. After the RTA process inter-device variability and intra-device stability in contact resistance decreased; more stable, consistent contacts were formed. This is in part due to decreased residue but also from smaller grain sizes forming producing a higher quality contact [77].

In-situ current annealing presents an alternative, less damaging annealing option. A large

current is passed through the graphene channel, resulting in Joule heating as would be desired in a normal annealing process allow for the desorption of any adsorbed contaminants from the channel. The surface contaminants can cause charge doping or act as scattering sites [97]. Although the SiO₂ support used can also act as a charge donor and scattering site. Other works have also used Joule heating to anneal graphene and remove contaminants, even able to remove CdSe NPs [99].

As was discussed previously, many methods have been attempted to remove residue from graphene. Those processes, as outlined, can cause undesirable damage to the sensitive graphene; instead processes which mitigate the residue should be considered. Hence, aluminium sacrificial layers have been utilised to protect the graphene during photolithography steps due to its ease of removal. Although it may result in additional defects and edge sites in the graphene [100]. The use of Al sacrificial layers on CVD-G has facilitated reduction in contact resistance from $2 \rightarrow 0.5 k\Omega\mu m$ and reduced sample roughness: only PMMA residue is present. The use of Al sacrificial layers is scalable unlike less destructive cleaning processes, which is critical for the higher throughput CVD-G material, which retains more residue due to its intrinsic defect density and wrinkled structure. Al protective layers complement CVD-G [101]. Like Al sacrificial layers, the final contact metal can instead be used to protect the graphene which is then selectively removed in photolithographic processes to define the device geometry. This has achieved contact resistance reduction as much as 60% [102].

B.4 Graphene Contact Approaches

Contacting graphene is known to alter its charge doping due to its low density of states, which is demonstrated through photocurrent microscopy demonstrating the presence of a potential step and built in electric fields. It is also shown that the sheet is p-doped at the sheet edges but n-doped at the centre [103]. The observed built-in electric fields only add to the injection barriers experienced by metal contacts, consequentially two broad methods were developed to mitigate these factors. Doping to minimise the pn-junction formation as already discussed and edge contacting to subvert the Schottky barrier. Fundamental to the understanding of edge contacts is structures with only edge contacts without top or bottom contacts being formed, which has been achieved in all CVD grown methodologies with hBN encapsulated graphene insulating its top and bottom surfaces. The hBN also has minimal lattice mismatch [104].

Although edge contacting appears to be more promising due to its ability to directly access the graphene sheet top and bottom contacts are a more straightforward geometry to realise. Top and bottom contacts should be equivalent in how they contact the graphene, in a pristine, theoretical consideration. However, the influence of contaminants and scalability need to be considered. As previously noted, photolithography and CVD growth result in the presence of residue on graphene, although due to the top down nature more residue will be present at a top interface than at a protected, bottom interface. Further, in top contacting geometries it is necessary to locate the desired region for patterning, while in the case of CVD-G, bottom contacts result in a self-aligned configuration, maximising throughput. The use of bottom contacts with CVD-G results in a reduction in both contact resistance and variability relative to equivalent top contacts. This is likely due to the negation of the influence of interfacial contamination [105]. The use of bottom contacts to graphene reduces the interaction that the graphene could have with the substrate such as SiO₂. Similarly, an equivalent protection would be afforded in a double contact, with the additional benefit of protecting the top surface from environmental interactions [106].

Double contact structures are the combination of both top and bottom contacts and have resulted in odd behaviour, deviating from either that of top or bottom contacts. For example, Pt physisorbs onto graphene in either top or bottom contacts. The resulting contact experiences the expected charge injection barrier. However, when a double-sided contact is modelled

chemisorption occurs due to charge redistribution at the Pt/G/Pt interface. When the metal approaches the graphene, the surface work function changes on the metal due to Pauli exclusion. Electrons are then transferred according to the work function differences. In the case of a single sided contact a dipole is formed at the interface. While in a double-sided contact at large separation a small lift of the Pt Fermi level is experienced due to weak exclusion influences; simultaneous charge redistribution to account for the work function shift is experienced. At smaller separation, the exclusion influence increases further, and the work function of the Pt increases, and some electrons are transferred back. The presence of symmetric anti-parallel dipoles ensures that electrons are retained in the basal plane of the graphene and an accumulation layer forms.

Although the Pt d-orbital overlaps with the graphene p_z orbital, physisorption and not chemisorption occurs due to the influence of lattice mismatch. This is no longer the case due to charge redistribution; chemisorption occurs; direct transfer of charge can occur. The type of metal used is significant in these contacts. The two metal layers need to be either p-type or n-type charge acceptors/donors. For example, a Pt-G-Ti stack, no EAL forms, instead electrons are just transferred from Ti to Pt via the g, while for Pt-G-Pd an EAL forms and the charge injection barrier disappears [107]. Other works modelling double contacts in the form of adlayers similarly observe enhancement of Ni-G bonding and buckling of the graphene layer. Further, Cu–G–Ni stacks also demonstrate an enhancement, although less significant. These enhancements manifest as a larger than normal electron density [108]. The same work also observed that Ni–Cu–G and Cu–Ni–G metal stacks display the behaviour of the contact layer even if only an adlayer is present.

Although simpler to achieve through traditional lithography processes, top or bottom contacts are limited in the quality of the contact they can achieve to systems. This is notably due to the stacked sp^2 nature of graphene, presenting as parallel channels isolated from each other. Graphene is conductive in the plane but insulating between its layers. So, to access layers of graphene that are not directly contacted on the surface, tunnelling must occur; increasing their access resistance. Further in the case of GFETs structures, layers of graphene distant from the gate experience less modulation due to screening effects of the intermediary layers. The result

of these influences is that the reduction in resistance afforded by multilayer saturates quickly due to the necessary tunnelling; only the first two layers are essentially used. This extends even when edge contacting is used for the source and drain as the modulation of the gate is still attenuated quickly [109]. As such the discussion is returned to the difficult to achieve but more promising edge contacting geometry. Direct comparisons between edge and side contacting geometries have been demonstrated for several metals (Ti, Pd, Pt, Cu, Au) in each case lower contact resistances were achieved in the edge contact. In part this is due to the facilitation of direct bonding as previously noted, but also due to better geometrical overlap of orbitals [110].

The reduction in contact resistance afforded by carbide bond formation between metals and high energy edge sites has great potential for optimising metallisation of graphene. However, pristine graphene samples have limited available sites for such bonding, CVD-G contains known surface defects that can allow for carbide formation. The presence of interfacial residues can prevent access to these sites. Consequently, the use of plasma treatments to remove the residue allowed for the observation that partial damage to the graphene surface can produce high energy sites prone to carbide formation. This leads to low contact resistance upon annealing. The plasma treatment can oxidise the graphene damaging its material properties. Despite this, the facilitated bonding removes the tunnelling barrier and decreases the metal-graphene separation decreasing the contact resistance [111].

Noting that contact resistance is reduced in edge-contacted structures inspired works to investigate the scaling of contact resistance with increasing number of edge sites being available. These include structures containing combed teeth structures, whereby structures with more finely spaced combs (greater perimeter) had lower contact resistances [85]. Similarly, other works have used long cut structure normal to the direction of charge transfer to decrease contact resistance [112]. Both works were seen to further vary on the doping profiles of the materials used, although that is not the main focus of this current discussion. The use of combs and cuts structures to increase available edge site inspired further approaches to enhance the availability of edge-contact sites.

Self-assembling catalysed etches into the graphene have been investigated to replace top down patterning methods. Successes have been achieved using Co-mediated etches with good

crystallographic etch control as well as with pit size control based on thickness of deposited Ni films. In each of these cases initial metal deposition, followed by an anneal to achieve islands/beads of metal were used to define the sites that could then be etched. In the case of Co, pre-patterning of the Co was used to control the sites etched achieving zig-zag terminations. While, the beading seen for Ni would determine the distribution of etched sites. Both methods achieved increased availability of edges for further contacting [95, 113].

These catalysed etch methods, despite requiring less intervention and process steps produce greater variability in the surface and thus contacts formed. As such more traditional methodologies were used. e-Beam/Oxygen plasma etch processes were used to form arrays of holes in graphene with differing perimeter sizes, noting decreasing contact resistance and current crowding (longer transfer lengths, more efficient use of contact area) [114]. Lithographic etches of holes produced contacts with high covalent bonding between the metal and graphene at the hole perimeter graphene edge sites, reducing the contact resistance. With smaller diameter holes, decreasing the contact resistance more, greater density of edge sites possible with smaller holes [115]. Further work under the same methodology suggested that the denser grid of small holes results in a more metallic electrostatic potential, achieving lower contact resistance [116]. As such, this is a critical region of interest for not only transistor designs but for all graphene-based technologies. Given that contact resistance is a significant challenge even for semiconductor MOX-based VOC sensors (section 1.4.3). For LIG based VOC sensors this high contact resistance would diminish the observable responses decreasing the sensor sensitivity and LOD. In traditional semiconductor device fabrication, contact resistance is well understood, with origins including differences in band structures, p-n junction formation and injection barriers.

C.1 Raman Spectroscopy Theory

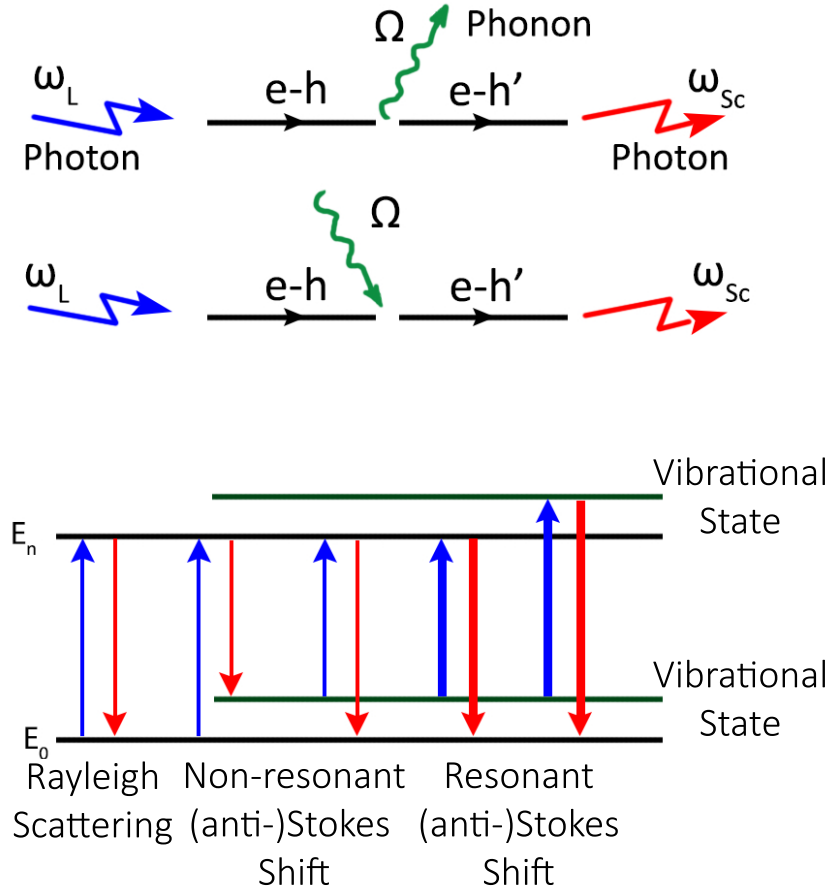


Figure C.1: (Top) Stokes shift; an incoming photon ω_L excites an electron-hole pair e-h. The pair decays into a phonon Ω and another electron-hole pair e-h'. The latter recombines, emitting a photon ω_{sc} . (Middle) Antistokes; the phonon is absorbed by the e-h pair. (Bottom) Rayleigh and Raman scattering in resonant and non-resonant conditions. [117]

When a photon of light is incident on an electron in a molecule it acts as a quantum of energy, $\hbar\omega_L$. This results in the excitation of the electron to an excited state, relaxation occurs and the electron then returns to its ground state energy (E_{gs}), re-emitting the energy difference as a photon of the same energy it absorbed. This classical consideration is known as Rayleigh scattering. The photon energy is conserved. This is the dominant mechanism in the interaction of light and matter; however, it is not the only possible outcome. For example, if the electron is in an excited vibrational state when the photon is incident, then the photon emitted when

the electron relaxes to its ground state would be at a higher energy than the original incident photon. Similarly, if the electron that was excited from its ground state relaxes to an energy state higher than its ground energy then the emitted photon is of a lower energy than the excitation photon. The changes in frequency are known as the anti-stokes and stokes shift respectively. The changes in energy observed are due to interactions with phonons of the material. These are minority interactions relative to the Rayleigh scattering due to their low probability and orbital overlap, further anti-stokes shifts are again less likely to occur than a stokes shift due to the low population of the vibrational state under normal conditions of temperature.

It is not necessary for the excitation state to be a real energy level. Instead a virtual state, force oscillation of electrons, can temporarily hold the electrons, although with a shorter lifetime. More formally Rayleigh scattering occurs when $\Delta\omega_l = 0$ while Raman scattering occurs when $\Delta\omega_l \neq 0$ such that the frequency of the oscillation Ω is defined by $\hbar\omega_L - \hbar\omega_{sc} = \hbar\Omega$. Although possible, Raman scattering mediated through virtual states is less efficient than through stationary states, known as resonant Raman. Due to the wavelengths of light used, (IR,UV) electronic excitation is an intermediate step, instead of direct photon-phonon coupling as laser energy $\gg$ than phonon energy. Raman spectroscopy informs both electronic and vibrational structure information of the material. As their structure defines the available states the excited electron can occupy.

Further description of the Raman process and how it impacts on graphene and graphene-like materials will be described in three complementary forms; quantum mechanical perturbation theory, real-space interactions and in terms of symmetry. Each of these methods provide further insight into why, unlike more general materials the potential density of states isn't reproduced, instead a sparsely populated spectrum with sharp peaks is formed. This is due to graphene's linear, gapless electronic dispersion allowing for any ω_L , lack of excitons and in the wavelength range, symmetric conduction and valence bands ($m_h \approx m_e$). For the consideration of the mechanism of Raman scattering the following notation is defined:

- $\vec{K}_l, \omega_L = cK_l$ Wave vector and frequency of incoming photon
- $\vec{K}_{sc}, \omega_{sc} = cK_{sc}$ Wave vector and frequency of scattered photon

- q, Ω_q^ν ; Wave vector and frequency for phonon branch ν

Hence $\omega_L = \omega_{sc} \pm \Omega_q^\nu$, $K_L = K_{sc} \pm q$, in other words; Stokes shifts result in the formation of phonons, anti-stokes shifts result in their annihilation. Again considering the wavelengths used in Raman [230, 1060] nm and the lattice parameter of graphene ($a \sim 1.42\text{\AA}$) it is seen that $K_L, K_{sc} \ll \frac{\pi}{a}$; $q \ll \frac{\pi}{a}$ [117].

As in any process involving electron excitation an electron and hole pair is created. For a photon to be re-emitted it is necessary for pair recombination to occur it is necessary for the two charge carriers to be in the same location. In other words, the momentum change due to the phonon interaction, q , should be approximately zero. This is known as the fundamental selection rule. For first order scattering processes (one phonon) this heavily restricts the potential wavelengths to just that near the Γ point for graphene. Although in graphite there are separately available phonons due to interlayer coupling and out of plane modes. A key distinction in their Raman spectra. However, higher order processes with phonon combinations such that the net momentum change is zero are allowed. The most common formation of this is a Double resonance processes. Whereby, any two phonons of opposite wave vector such that $\vec{q} + (-\vec{q}) = 0$ can be used. As such all phonons can contribute to a multi-phonon processes and should reproduce the Phonon Density of States (PDOS) [117].

However, this general behaviour is not true for graphene. The features seen for graphene are scarce, not like those of its PDOS. This is due to several additional factors influencing the allowedness of given interactions including resonance processes, electron-phonon and electron-electron interactions. This can be considered formally through perturbation theory and transition moment integrals. For example, consider an arbitrary Raman process with n intermediary states. The transfer between the initial and final stationary states can be described by the matrix element in Equ. C.1. If any of the transitions are disallowed then the corresponding probability of the transition becomes approximately zero. If any of the energy differences in the denominator become approximately zero then resonant behaviour and peaks are observed in the probability. Terms can add constructively or destructively in sum. They are complex amplitudes of the corresponding elementary process with given intermediate states [117].

$$\mathcal{M} = \sum_{s_0, \dots, s_n} \frac{\langle f | \hat{H}^{em} | s_n \rangle \langle s_n | \hat{H}^{ph} | s_{n-1} \rangle \dots \langle s_1 | \hat{H}^{ph} | s_0 \rangle \langle s_0 | \hat{H}^{em} | i \rangle}{(\hbar\omega_L - E_n + i\Gamma_n/2) \dots (\hbar\omega_L - E_1 + i\Gamma_1/2) (\hbar\omega_L - E_0 + i\Gamma_0/2)} \quad (\text{C.1})$$

Where $|i\rangle$ is the initial state, n phonons left in the crystal, $|f\rangle$ final state, $s_k, k = 0, \dots, n$ intermediate states without photons. e-h pair is created and K phonons emitted $E_k, \Gamma_k/\hbar$ Energies and decay rates of the intermediating states. $\hat{H}^{em}, \hat{H}^{ph}$ Hamiltonian describing interaction of electrons with electromagnetic field and phonons [117].

This consideration can also be extended to account for the presence of defects in the material under study by treating the of phonons of zero frequency that elastically scatter. This can further allow any previously excluded phonons to produce defect assisted peaks where the defects account for the phonon momentum. The matrix element $\mathcal{M}$ then describes the intensity of the peak associated with a given phonon as described by Equ. C.2. The peak area can also be described by Equ. C.3 [117].

$$I(\omega_{sc}) \propto \int |\mathcal{M}|^2 \delta(\Omega_{q1}^{\nu_1} + \dots + \Omega_{qn}^{\nu_n} - \omega_{sc}) d^2 q_1 \dots d^2 q_n \quad (\text{C.2})$$

$$A \propto \int I(\omega_{sc}) d\omega_{sc} \quad (\text{C.3})$$

Where: $q_1, \dots, q_n$ Wavevectors of emitted phonons, $\nu_1, \dots, \nu_n$ Branch labels, $\Omega_{q1}^{\nu_1}, \dots, \Omega_{qn}^{\nu_n}$ Their frequencies. Formally, for dispersion-less, undamped phonons Ω^ν : Phonon peaks' shape $\propto \delta(\omega_{sc} - n\Omega^\nu)$ with zero width and infinite height. However, if defects are present, as expected in any physical system the Dirac Delta structure is lost and a Lorentzian is observed. [117]

The real-space consideration of Raman processes assists in the determination of why the PDOS isn't purely reproduced. Firstly, the validity of the modelling the interactions as a real space process can be established by considering the magnitudes of the energies involved. For visible Raman experiments the electronic energy $\epsilon \approx \frac{\hbar\omega_L}{2} \sim 1 \text{ eV}$ and in a double-resonant process the phonon energies near Γ, K, K' is $0.17 - 0.2 \text{ eV}$. Therefore, from the uncertainty principle; lifetime of intermediate state $\sim \hbar/\delta\epsilon$. The spatial extent is thus $l = \frac{\hbar v_F}{\delta\epsilon}$ the spatial extent, where the, Fermi velocity, $v_F = 10^8 \text{ cm s}^{-1}$. $l \sim \frac{v_F}{\Omega} \sim 3.5 \text{ nm}$, $l \gg \frac{\hbar v_F}{\epsilon} = 0.7 \text{ nm}$. The spatial extent $\gg$ the electron wavelength [117].

So the electron and hole motion can be viewed as quasi-classical. Consequently, in a classical consideration, only phonon interaction processes that result in the electron and hole recombining at the same point can result in a photon emission. Phonon interactions must result in the backscattering of the phonon. Hence zero-momentum phonons cannot interact in a double resonance process. Therefore, no 2G peak is observed. Further, as the velocities of electrons and holes in graphene are almost the same, then an additional restriction can be considered, electron and holes must travel for the same amount of time for the emission to occur. Although forbidden in the physical process ee or hh processes that would require one carrier to travel further, in the broader QM model they are allowed, although with reduced intensity. The observation of these peaks at all, is assigned to the high electron-phonon coupling and their broad nature [117].

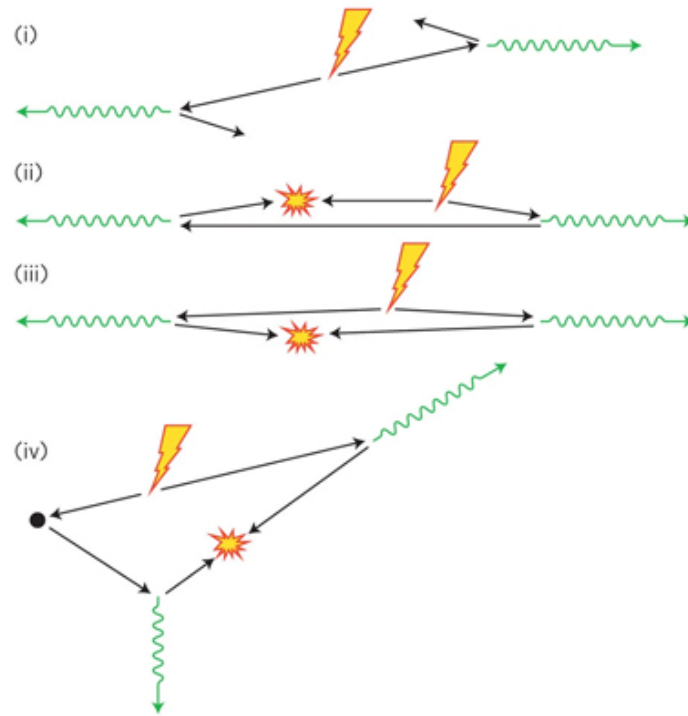


Figure C.2: Real-Space Raman consideration. i) Disallowed Raman processes, as interacting phonon result in eh pair that never collide, ii) Disallowed ee Raman process as interacting with phonons despite causing backscattering do not result in equal path lengths. iii) Allowed Raman process, as interacting with phonons cause backscattering with equal path lengths. iv) Defect assisted Raman scattering. Reproduced from *Ferrari et al.* [117]

In the case of samples that contain defects, first order peaks with non-zero momentum can then be observed as the momentum can be accounted for by the defect sites. Similarly, higher order defect peaks can also occur. The introduction of defects removes the requirement of the backscattering condition. Consequently, $Pos(D + D') \neq Pos(D) + Pos(D')$ as the phonon

allowed in the process can occur at a wider range of frequencies. Similarly defect assisted peaks will be broader than non-defect mediated peaks as a broader allowed range of phonons resulting in a broader peak. [117]

The use of perturbation theory and real space considerations so far have informed both the line shapes of the peaks, their allowedness and interaction with defects. However, this has largely been discussed in terms of planar graphene, point group theory can be used to schematically support these results and to extend the understanding to multilayer systems. As the materials to be studied in this work are not pristine 2D hexagonal lattice of carbon atoms as previously assumed. However, it is beneficial to begin the discussion in terms of the graphene two-point basis unit cell of atoms A and B displaced by 0.142 nm. Forming a lattice of constant $a=0.246$ nm corresponding to the Brillouin Zone (BZ) shown in Figure C.3a [118]. Each atom contributes four valence electrons, three of which form the sp^2 bonds and the remainders join the π -electron system. The two atoms per unit cell result in six branches of phonons to consider, three of which are acoustic and three optical, and are orientated along the high symmetry directions ΓM and ΓK . They are in-plane Longitudinal Acoustic (iLA), in-plane Transverse Acoustic (iTA), out-of-plane Transverse Acoustic (oTA), iLO, iTO and out-of-plane Transverse Optical (oTO) as shown in Figure C.3b.

The most important features of the phonon dispersion are the kink in the iTO at the K point and the positive slope of the iLO branch at Γ . These are the previously mentioned Kohn anomalies; regions where the phonon energy of a given wave vector is lower relative to other parts of its band in the local region. They are caused by the presence of the Fermi surface of graphene at K and K' in the BZ. Therefore the wave vector at these points produces a decreased screening of ionic charge resulting in an enhancement of the electron-phonon interaction reducing the energy of the corresponding phonons [121].

The addition of layers to the Monolayer Graphene (MG) provides additional degrees of freedom to both the phonon and electronic dispersion bands in the BZ. The transformation of MG to BG results in a small splitting of the band structure into new modes corresponding to the in-phase and out of phase motion of the two graphene sheets. A similar splitting of the electronic band structure is seen, whereby the previously single valence and conduction bands are split into

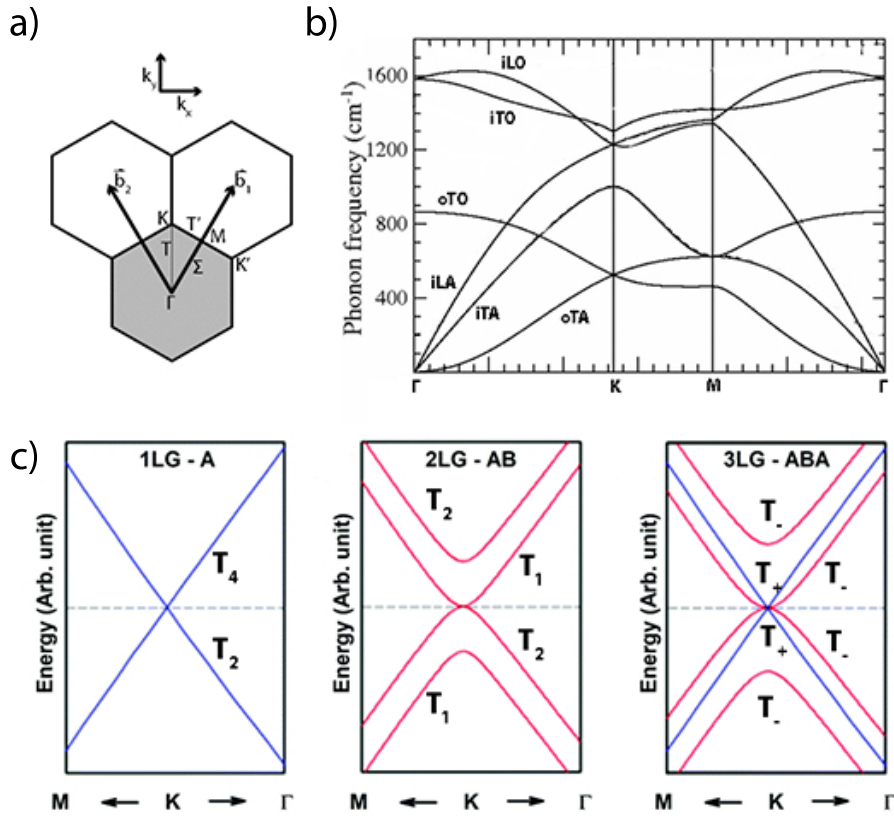


Figure C.3: Brillouin zone features of graphene. a). First Brillouin zone of graphene, with high symmetry points. b). Graphene phonon dispersion Adapted with permission from ref. [119]. c). Graphene Electron dispersion near K point Adapted from ref. [120].

symmetric and antisymmetric bands as shown in Figure C.3c. By considering different regions of the BZ in terms of Point Group Theory it is possible to determine the symmetry groups to which the high symmetry points of the BZ are isomorphic. It is also seen in this treatment that even numbered layers of Few-Layer Graphene (FLG) and odd numbered layered FLG belong to the same symmetry group as the BG and TG respectively. It is sufficient to analyse just these three structures for a qualitative understanding of FLG [122]. The point group that each material is isomorphic to; as a bulk and the sub groups for high symmetry points are given in Table C.1.

The deviation of the even and odd layer terms from that of the MG or the bulk is caused by their lack of the horizontal mirror plane and the inversion operation respectively and therefore belongs to different point groups. A requirement for a vibrational mode to be Raman active is that it results in a change in the polarizability, this only occurs if the irreducible representation

Table C.1: Isomorphic point groups of high symmetry points of monolayer, N-layer graphene and graphite.

	Shchoenflies Space Group	Γ	$K (K')$	$T(T')$
Monolayer	P6/mmm	D_{6h}	D_{3h}	C_{2v}
N Even	$P\bar{3}m1$	D_{3d}	D_3	C_2
N Odd	$P\bar{6}m2$	D_{3h}	C_{3h}	C_{1h}
Graphite	$P6_3/mmc$	D_{6h}	D_{3h}	C_{2v}

of the vibration is a second order basis function. Consequently, Point Group Theory can be used to predict potential Raman mode frequencies. The possible Raman active irreducible representations for phonons near the Γ point and along the T/T' shown in Table C.2 Similarly the symmetries of the π electron band structure for each of the materials near the Γ point and along the T/T' line is also given in Table C.2 in Bethe Notation.

Table C.2: Irreducible representations of lattice vibrations and π electronic band structure near the Gamma point and along the T line of monolayer and N-layer graphene.

Phonon Symmetries			
	Monolayer	Bilayer	Trilayer
Γ	$\Gamma_2^- + \Gamma_5^- + \Gamma_4^+ + \Gamma_6^+$	$2(\Gamma_1^+ + \Gamma_3^+ + \Gamma_2^- + \Gamma_3^-)$	$2\Gamma_1^+ + 4\Gamma_2^- + 4\Gamma_3^+ + 2\Gamma_3^-$
$T(T^-)$	$2T_1 + T_2 + 2T_3 + T_4$	$6(T_1 + T_2)$	$10T^+ + 8T^-$
π Electron Band Symmetry			
	Monolayer	Bilayer	Trilayer
$T(T^-)$	$T_2 + T_4$	$2(T_1 + T_2)$	$2T^+ + 4T^-$

As previously outlined, Stokes shifts occur due to an inelastic scattering of light, which occurs when phonons interact with electrons that have been excited from valence band to the conduction band by incident light. It is then possible for a phonon to interact with the excited electron, either increasing/decreasing the energy and possibly altering the momentum depending on the wave vector of the phonon. Similarly, as noted in the real-space consideration, the conservation of momentum it is necessary for any Stokes shift process to have a net zero momentum change. This can occur in several ways including; an incident phonon of zero wave vector, a pair of phonons with equal wave vectors or a phonon and a scattering from a defect that can account for the momentum through elastic scattering.

The simplest of these is that of a zero valued wave vector, known as a first order process. In this process an electron of wave vector $\mathbf{k}$, that has been excited to the conduction band, interacts with a phonon from the Γ point resulting in an energy change. It then recombines with a hole of

wave vector $\mathbf{k}$ emitting a photon of a different energy than had been absorbed, due to the energy associated with the phonon interaction. The other processes occur through a more complex DR process involving an initial electron of wave vector $\mathbf{k}$ around the K point of the BZ that absorbs a photon and is promoted into a conduction band. The electron is then scattered inelastically by a phonon or defect of wave vector $\mathbf{q}$ to a point around K' with wave vector $\mathbf{k}+\mathbf{q}$. The electron is then scattered back to the $\mathbf{k}$ state by a phonon or defect and emits a photon by recombining with a hole at a $\mathbf{k}$ state, as previously seen the energy of the resulting photon is shifted from that of the incident photon. The DR shift allows for the changing of the energy due to both phonons, or by only one phonon if it is a defect assisted process, as scattering by defects is elastic.

Table C.3: Symmetry allowed electronic transitions in monolayer and N-layer graphene.

	Polarisation	Transition Moments
Monolayer	$x \in T_3$	$T_2 \otimes T_3 \otimes T_4$
E Even	$x \in T_2$	$T_1 \otimes T_2 \otimes T_2$
	$y \in T_1$	$T_2 \otimes T_2 \otimes T_1$
		$T_1 \otimes T_1 \otimes T_1$
		$T_2 \otimes T_1 \otimes T_2$
N Odd	$x, y \in T^+$	$T^+ \otimes T^+ \otimes T^+$
		$4(T^- \otimes T^+ \otimes T^-)$

In both first order and DR Raman scattering, the process can only occur if an electron can be excited from a valence band to a conduction band by incident light of a given polarisation. The allowed processes can be determined by finding the direct product of irreducible representations of the initial valence band, light of a given polarisation and the final conduction band. The allowed electronic transition for MG, BG and TG are included in Table C.3. For the first order process the only other requirement is that a non-zero energy phonon exists with zero wave vector, to conserve momentum. In the case of MG, of the possible Raman active phonons, only that of the doubly degenerate Γ_6^+ has a non-zero energy at the Γ point. This corresponds to iLO and iTO in the phonon dispersion of MG and results in a peak being observed at $\approx 1580\text{cm}^{-1}$, known as the G peak. Due to the further dispersion and splitting of the phonon band structure caused by the addition of layers it can be seen that the corresponding wave vectors for BG and TG deviate from that of MG as given in Table C.4. Both producing the previously observed G peak with

additional peaks at $35 - 50\text{cm}^{-1}$, 80cm^{-1} and 900cm^{-1} caused by the splitting in their band structures.

For a process to occur in a DR process there is a different requirement; a phonon must have a non-zero wave vector so as to cause the scattering of the electron in the conduction band to another, symmetry allowed, conduction band near the point K'. Therefore only phonons that would result in a transfer to a symmetry allowed conduction band can take part in a DR process, these are shown in Table 6. They are found by taking the direct product of the irreducible representations of the initial conduction band and the incident phonon and comparing them to the symmetries of allowed conduction bands at the K' point.

Table C.4: Irreducible representation of phonon modes responsible for the G peak in monolayer and N-layer graphene.

Monolayer	N Even	N Odd
Γ_6^+	$\Gamma_3^+ + 2\Gamma_1^+$	$3\Gamma_3^+ + 2(\Gamma_3^- + \Gamma_1^+)$

For a process to occur in a DR process there is a different requirement; a phonon must have a non-zero wave vector so as to cause the scattering of the electron in the conduction band to another, symmetry allowed, conduction band near the point K'. Therefore only phonons that would result in a transfer to a symmetry allowed conduction band can take part in a DR process, these are shown in Table C.5. They are found by taking the direct product of the irreducible representations of the initial conduction band and the incident phonon and comparing them to the symmetries of allowed conduction bands at the K' point.

Table C.5: Symmetry allowed phonon transitions between symmetry allowed conduction bands in monolayer and N-layer graphene.

	Phonon Symmetries	Allowed Transition Processes
Monolayer	T_1	$T_4 \rightarrow T_4$
N Even	T_1	$T_1 \rightarrow T_1, T_2 \rightarrow T_2$
	T_2	$T_1 \rightarrow T_2, T_2 \rightarrow T_1$
N Odd	T^+	$T^+ \rightarrow T^+, T^- \rightarrow T^-$
	T^-	$T^+ \rightarrow T^-$

Considering the case of the 2D peak in BG, due to the dispersion caused by the additional graphene layer, its electronic dispersion band structure contains four bands near the K/K' point,

as shown in Figure C.3c. From the allowed electronic transitions in Table C.3 it is seen that either of the valence bands can be excited to either of the conduction bands, resulting in two symmetry allowed conduction bands for DR Raman scattering. For these bands there are two phonon symmetries that can produce symmetry allowed electronic bands at the K' point through four possible pathways as shown in Table C.5. The electron is then scattered back to its initial wave vector by another phonon, obeying the symmetry rules, resulting in two energy shifts, one due to each phonon and each of the four pathways possessing discrete energy shifts.

A similar analysis can be carried out for MG or TG, which produce bands constructed from one and 15 peaks respectively. Showing that the dispersion caused by layer number can be directly linked to peak shape. Due to the similar energies of the resulting peaks they overlap to produce a net band feature in the Raman spectrum of characteristic width and intensity. Defect assisted processes can be similarly considered, where one of the phonon processes is replaced by an elastic defect scattering conserving momentum but not producing a Stokes shift. Although the DR condition can be satisfied by many electronic states and phonons, the presence of the Kohn anomalies results in an amplification of wave vectors in those regions. This results in characteristic energies of the resulting peaks in graphene. In MG the iTO phonon band obeys the symmetry requirements of the DR process at the K point and results in the production of a band at $\approx 2700\text{cm}^{-1}$ corresponding to twice the energy of the phonon at that point. As such it is known as the 2D band. In BG and TG the corresponding dispersed iTO bands produce their 2D feature, with the previously outlined splitting. If defects are present in the sample additional peaks are seen at $\approx 1350\text{cm}^{-1}$ which corresponds to the same phonons but occurs through a pathway using an elastic defect scattering step. This is known as the D peak. Other peaks can also be formed following these symmetry rules such as the D' defect assisted band at 1600cm^{-1} which, also features a Kohn anomaly and corresponds to iLO near the Γ point. Additional peaks made from two phonons of different wave vectors can also be formed in the presence of defects accounting for the remaining momentum such as the $D + D'$ peak at 2950cm^{-1} .

D- EXPERIMENTAL METHODS

Include here are brief synopses of different methods used during this work. This augments the specific descriptions included in experimental chapters.

D.1 Laser Engraver

Current works focus on the use of a PLS 4.75 (Universal Laser System, 30 W 10.6 μm) CO₂ laser engraver for patterning polyimide samples. Other diode-based lasers at 450 nm and 405 nm are also available for use but are not currently a focus of the work. The laser itself follows the traditional mode of operation of a CO₂ laser. In a sealed tube a concentration of CO₂ and N₂ gases, as well as other filler gases such as He are placed at low pressure. The choices of CO₂ and N₂ are due to their energy level alignment between the N₂ excited state and the CO₂ asymmetric vibrational state which allows for transfer between the two states and the excitation of the CO₂ states. The decay of the CO₂ state to either of its symmetric or bending states results in the emission of a photon of wavelength 10.6 μm and 9.6 μm respectively. Population inversion of this type of laser depends on the excitation of the nitrogen vibrational modes through electric discharge, which are meta stable and long lived. Consequently, this long lifetime allows for collisions between the nitrogen and the CO₂ which would result in the transfer of the energy to the CO₂ molecule and the excitation to the asymmetric mode. The CO₂ then relaxes to the symmetric stretch or bending mode with photon emission. Further relaxation is then achieved by collisions with He atoms. The He atoms transfer this energy in the form of heat to the walls of the laser for external cooling. Tuning of gas ratios and pressures is used to select for the desired 10.6 μm wavelength.

The emitted light is reflected back and forth between two mirrors of reflectivity $R \approx 1$ and $R < 1$ and a coherent laser beam emitted through the lower reflectivity mirror as required. Separately to the laser component are additional electronics, such as a shutter allowing for the beam to be stopped and pulsed, x and y-axis stepper motors, a z-axis platen adjustable by screw drive motors and laser focusing optics. Additionally, air extract is included to protect the laser optics from redeposited material. These components allow for control over numerous laser

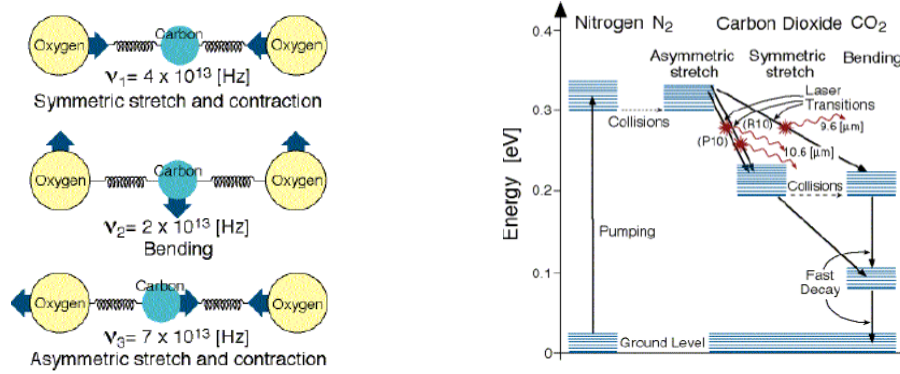


Figure D.1: (Left) Vibrational modes of CO₂ (Right) Excitation mechanism of CO₂ gain mode laser.

parameters including laser power, scan speed, horizontal pulse density, laser overlap, row density and laser focal plane.

D.2 Scanning Electron Microscope

SEMs operate similarly to traditional optical microscopes but instead of photons, electrons are instead accelerated from an electron gun towards the sample of interest. Under vacuum and using electromagnetic lenses, the electron beam is focused and then with further electromagnets it is deflected in the x and y directions to raster across the sample. The electrons that are scattered by the sample are collected by detectors and used to build up an image of the sample. The electrons can interact with the sample by also producing secondary electrons and characteristic x-rays that can also be used to produce the image. Although further depth and rigour is possible in the discussion of the operation of SEM it is not necessary for the use of the method or the interpretation of the resulting micrographs; it will be neglected at this stage.

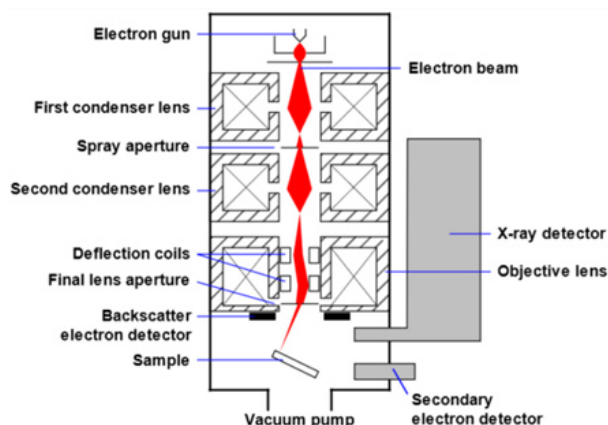


Figure D.2: Scanning electron microscope focusing electromagnetic lenses. Adapted from <https://www.nanoscience.com>

D.3 Fluorescence Microscopy

As was noted in the description of Raman spectroscopy, more than just Rayleigh scattering can occur when light interacts with a material resulting in excitation. For example, other relaxation processes can occur resulting in different energy photons being emitted. Depending on the process and the spins of electrons involved the lifetimes of the decays differ. For spin forbidden processes it is called phosphorescence, while for spin allowed processes it is called fluorescence. As can be seen in the Jablonski diagram, the expected process for fluorescence is that the excitation takes the electron to a high vibration state of the higher electronic energy level. Non-specular relaxation through the vibrational states takes place until the ground vibrational state is reached. From the lowest vibrational state specular relaxation occurs, with associated photon emission to a vibrational level of the electronic ground state with potential further non-specular relaxation occurring. This would allow insight into the electronic and vibrational energy levels to be derived, similarly potential photochemical roles or applications can be devised. To investigate this behaviour a fluorescence microscope is used with filter cubes to control the incident and monitored frequencies of light.

Jablonski Diagram

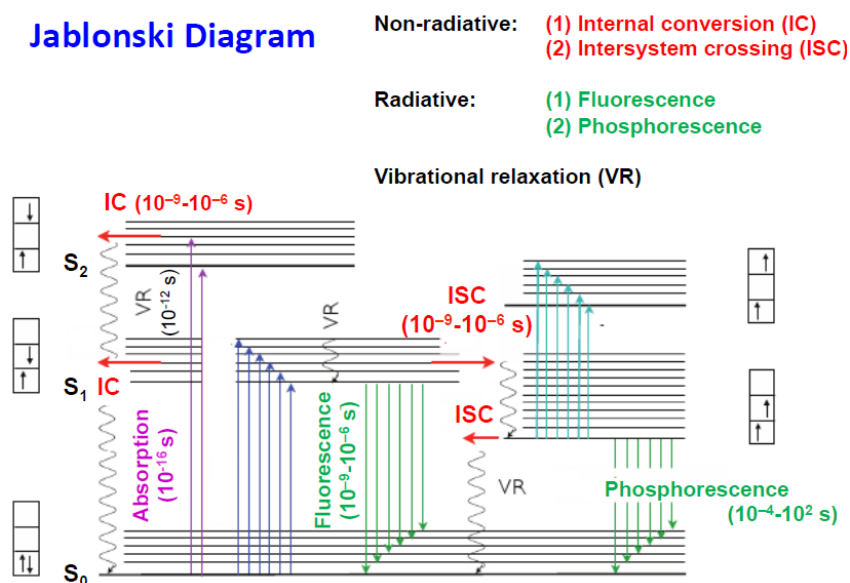


Figure D.3: Jablonski diagram indicating excitation and relaxation modes leading to fluorescence.

D.4 Design of Experiments

DoE is a statistical method used in optimisation processes. It uses ANOVA test statistics to determine the significance of variables on responses. However, unlike OFAT processes, DoE instead varies multiple factors simultaneously. This not only results in a reduction of necessary experiments but also allows for the consideration of multi-factor interactions. Key to the DoE method is the selection and consideration of factors, as each additional factor increases the number of samples to be produced, increasing the expense of the experiment. Unlike traditional one- OFAT methods, whereby each individual factor needs to be investigated independently, DoE allows for the screening of potential factors quickly, with minimal sampling. This can be achieved by constructing a half-factorial experiment on a greater number of factors, this provides less rigour to the output but the ANOVA considerations for each factor can be used to determine whether they merit further study, in minimal experimental runs.

In all DoE processes several steps are taken to mitigate the influence of uncontrollable factors such as instrumental drift or user influence. These include the randomisation of run order of different factor level combination and the implementation of blocks of experiments where known, but unavoidable, variation sources exist such as choice of equipment or easily influenced batch processes. The mitigation of these influences can reveal previously masked effects and provide increased certainty in significant factors, although they can come at an increased experimental

cost.

Unlike OFAT methods, DoE also allows for the analysis and consideration of interaction between factors. This is achieved by extending the ANOVA treatment and F-score analysis to combinations of factors and indicating whether a given combination of factors has a statistically significant impact on a response variable and whether the combination should be further studied. This is where DoE allows for a major saving in resources compared to OFAT methods. The same experimental measurements used to evaluate the main factors can be further used to investigate if interactions between factors play a role in determining the response. While for OFAT methods each interaction would require independent investigation. Further, the complexity of investigating higher order interactions through standard methods are non-intuitive and unlikely to be captured in a complex, novel system. The resulting set of significant main- and interaction-factors form a model, predictive of the behaviour of the responses with the measured factors. The provided insight would allow for relationships between factors and responses to be determined, rapid optimisation of dominant factors, and deprioritisation of insignificant factors for further studies.

This is often sufficient for early analysis work, however, more complex optimisation routines based on DoE are possible, one such example is the Response Surface Method (RSM). Whereby, the standard factor level combinations are measured but additional points are added to the model at the centre and at the edges in a central composite design. As with the standard factorial DoE approach the main-effects and interactions can be examined, however, the RSM allows for non-linearity in the main and interaction-effects to be explored. This allows for more explicit consideration of the relationships and produces a response surface indicating the curvature. By setting desirability conditions for the responses and factors, optimal factor values can be predicted. These predictions are subject to in-line statistical significance tests to ensure statistical significance of their contribution to the model.

By use of screening DoE processes followed by RSM it is possible to rapidly predict optimal points for further study, which may be non-intuitive for OFAT methods. Due to the uncertainty in the formation pathway of LIG it is not known how for any given variation in the production method may influence its behaviour in observing a response in a novel application. Therefore, the use of DoE will allow for complex interactions to be captured with empirical significance.

D.5 National Instruments LabView

National Instruments LabView (LabView) is a graphical programming environment for controlling equipment and data manipulation. In the course of this work it has been used to control several pieces of equipment for specific applications. These include real time monitoring of sensor responses (Aglient Precision LCR E4980A) and I-V potential sweeps (Aglient multislot parameter analyser E5270). Not shown here is the back panel of the Parameter Analyser program, as the no drivers were available so it must be controlled directly using VISA commands. These developed applets and built executables are available at https://github.com/Murray-R/Lab_view.

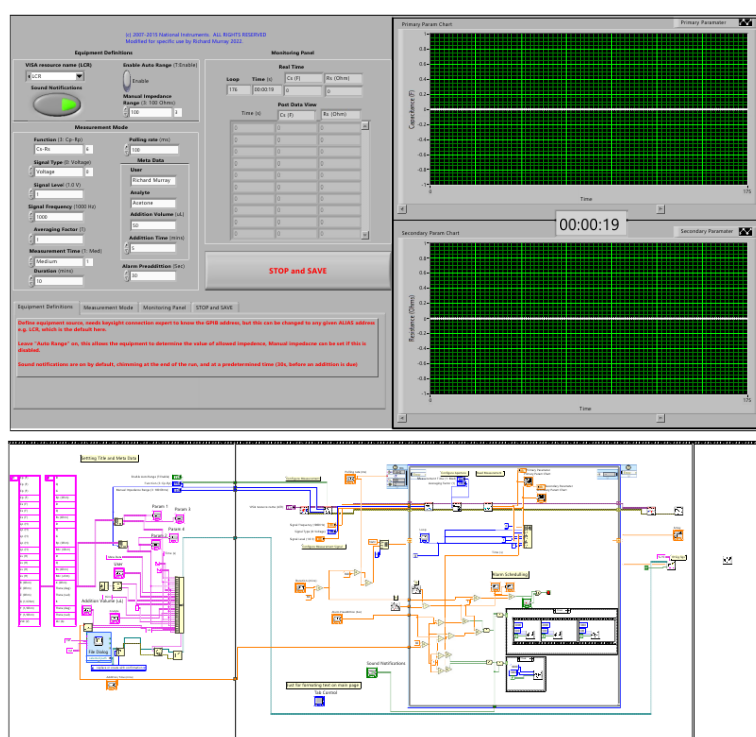


Figure D.4: Labview a) front and b) back panel representations of LCR control software for real time monitoring of gas sensing systems.



Figure D.5: Labview Front panel representation of Paramater analyser control software for determining the resistance of test structures.

D.6 3D Printing

During the course of this research work, custom experimental fixtures and fittings were required for experimental set ups. These were fabricated using a hobbyist FDM Crealty Ender 3, 3D printer. The .stl design files are freely available on Git-hub here: https://github.com/Murray-R/SnO_VOC_Sensor for reproduction. Available files include gas sensing chamber lids compatible with 50 ml centrifuge tubes, gas sensing chamber lids compatible with 600 ml wide-neck duran flasks, sample photography setups, as well as .stl files for other ongoing projects.

First Author Publications

- Murray, R., Burke, M., Iacopino, D., & Quinn, A. J. (2021). **Design of Experiments and Optimization of Laser-Induced Graphene**. ACS Omega, 6(26), 16736–16743.
<https://doi.org/10.1021/acsomega.1c00309>
- Murray, R., O'Neill, O., Vaughan, E., Iacopino, D., Blake, A., Lyons, C., O'Connell, D., O'Brien, J., & Quinn, A. J. (2022). **Direct-write formation of integrated bottom contacts to laser-induced graphene-like carbon**. Nanotechnology, 33(40).
<https://doi.org/10.1088/1361-6528/ac7c7b>

Targetting Publications

- Murray, R., Larrigy, C., Russo, A., Hoque, K., Iacopino, D., Quinn, A.J. **Room Temperature Sensing of Volatile Organic Compounds using Hybrid SnO nanoflowers and Laser-Induced Graphene-like Carbon Devices**

Additional Publications

- Imbrogno, A., Islam, J., Santillo, C., Castaldo, R., Sygellou, L., Larrigy, C., Murray, R., Vaughan, E., Hoque, M. K., Quinn, A. J., & Iacopino, D., (2022). **Laser-Induced Graphene Supercapacitors by Direct Laser Writing of Cork Natural Substrates**. ACS Applied Electronic Materials, 4(4), 1541–1551.
<https://doi.org/10.1021/acsaelm.1c01202>
- Paterakis, G., Vaughan, E., Gawade, D. R., Murray, R., Gorgolis, G., Matsalis, S., Anagnostopoulos, G., Buckley, J. L., O'Flynn, B., Quinn, A. J., Iacopino, D., & Galiotis, C., (2022). **Highly Sensitive and Ultra-Responsive Humidity Sensors Based on Graphene Oxide Active Layers and High Surface Area Laser-Induced Graphene Electrodes**. Nanomaterials, 12(15).
<https://doi.org/10.3390/nano12152684>
- Mu, Y., Islam, J., Murray, R., Larrigy, C., Russo, A., Zhang, X., Quinn, A.J., Iacopino, D., (2023) **Silver Nanoparticles-Laser Induced Graphene (Ag NPs-LIG) Hybrid Electrodes for Electrochemical-Surface Enhanced Raman Spectroscopy (EC-SERS) Detection**. Analyst, **148**, 3087-3096
<https://doi.org/10.1039/D3AN00731F>
- Hamidi, H., Levieux, J., Larrigy, C., Russo, A., Vaughan, E., Murray, R., Quinn, A.J., Iacopino, D., (2023) **Laser-Induced Graphene (LIG) Biosensors Derived from Chitosan: Towards Sustainable and Green Electronics**. preprint,
https://papers.ssrn.com/sol3/papers.cfm?abstract_id=4425608

BIBLIOGRAPHY

- [1] J. W. Yoon, J. K. Choi, and J. H. Lee, "Design of a highly sensitive and selective c 2h 5oh sensor using p-type co 3o 4 nanofibers," *Sensors and Actuators, B: Chemical*, vol. 161, no. 1, p. 570–577, 2012.
- [2] N. Barsan, C. Simion, T. Heine, S. Pokhrel, and U. Weimar, "Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors," *Journal of Electroceramics*, vol. 25, no. 1, p. 11–19, 2010.
- [3] M. Hübner, C. E. Simion, A. Tomescu-Stănoiu, S. Pokhrel, N. Bârsan, and U. Weimar, "Influence of humidity on co sensing with p-type cuo thick film gas sensors," *Sensors and Actuators, B: Chemical*, vol. 153, no. 2, p. 347–353, 2011.
- [4] S. Pokhrel, C. E. Simion, V. Quemener, N. Bârsan, and U. Weimar, "Investigations of conduction mechanism in cr2o3 gas sensing thick films by ac impedance spectroscopy and work function changes measurements," *Sensors and Actuators, B: Chemical*, vol. 133, no. 1, p. 78–83, 2008.
- [5] J. W. Yoon, H. J. Kim, I. D. Kim, and J. H. Lee, "Electronic sensitization of the response to c2h5oh of p-type nio nanofibers by fe doping," *Nanotechnology*, vol. 24, no. 44, 2013.
- [6] D. Degler, S. Rank, S. Müller, H. W. Pereira De Carvalho, J. D. Grunwaldt, U. Weimar, and N. Barsan, "Gold-Loaded Tin Dioxide Gas Sensing Materials: Mechanistic Insights and the Role of Gold Dispersion," *ACS Sensors*, vol. 1, no. 11, pp. 1322–1329, 2016.
- [7] M. Hubner, N. Bârsan, and U. Weimar, "Influences of al, pd and pt additives on the conduction mechanism as well as the surface and bulk properties of sno2 based polycrystalline thick film gas sensors," *Sensors and Actuators B: Chemical*, vol. 171–172, p. 172–180, 2012.
- [8] M. Hübner, D. Koziej, M. Bauer, N. Barsan, K. Kvashnina, M. D. Rossell, U. Weimar, and J. D. Grunwaldt, "The structure and behavior of platinum in sno2-based sensors under working conditions," *Angewandte Chemie - International Edition*, vol. 50, no. 12, p. 2841–2844, 2011.
- [9] M. Hübner, D. Koziej, J. D. Grunwaldt, U. Weimar, and N. Barsan, "An au clusters related spill-over sensitization mechanism in sno2-based gas sensors identified by operando herfd-xas, work function changes, dc resistance and catalytic conversion studies," *Physical Chemistry Chemical Physics*, vol. 14, no. 38, p. 13249–13254, 2012.
- [10] D. Degler, H. W. Pereira De Carvalho, K. Kvashnina, J. D. Grunwaldt, U. Weimar, and N. Barsan, "Structure and chemistry of surface-doped Pt:SnO2 gas sensing materials," *RSC Advances*, vol. 6, no. 34, pp. 28149–28155, 2016.
- [11] K. Großmann, S. Wicker, U. Weimar, and N. Barsan, "Impact of pt additives on the surface reactions between sno2, water vapour, co and h2; an operando investigation," *Phys. Chem. Chem. Phys*, vol. 15, p. 19151–19158, 2013.
- [12] N. Bârsan and U. Weimar, "Understanding the fundamental principles of metal oxide based gas sensors; the example of co sensing with sno 2 sensors in the presence of humidity," *J. Phys.: Condens. Matter*, vol. 15, p. 813–839, 2003.
- [13] X. Xue, Z. Chen, C. Ma, L. Xing, Y. Chen, Y. Wang, and T. Wang, "One-step synthesis and gas-sensing characteristics of uniformly loaded pt@sno2 nanorods," *Journal of Physical Chemistry C*, vol. 114, p. 3968–3972, 2010.
- [14] X. Kou, F. Meng, K. Chen, T. Wang, P. Sun, F. Liu, X. Yan, Y. Sun, F. Liu, K. Shimanoe, and G. Lu, "High-performance acetone gas sensor based on ru-doped sno2 nanofibers," *Sensors and Actuators, B: Chemical*, vol. 320, no. May, 2020.
- [15] M. Kugishima, K. Shimanoe, and N. Yamazoe, "C2h4o sensing properties for thick film sensor using la2o3-modified sno2," *Sensors and Actuators, B: Chemical*, vol. 118, no. 1–2, p. 171–176, 2006.
- [16] P. K. Dutta, A. Ginwalla, B. Hogg, B. R. Patton, B. Chwierothe, Z. Liang, P. Gouma, M. Mills, and S. Akbar, "Interaction of carbon monoxide with anatase surfaces at high temperatures: Optimization of a carbon monoxide sensor," *Journal of Physical Chemistry B*, vol. 103, no. 21, p. 4412–4422, 1999.

- [17] C. Imawan, F. Solzbacher, H. Steffes, and E. Obermeier, "Gas-sensing characteristics of modified-moo3 thin films using ti-overlayers for nh3 gas sensors," *Sensors and Actuators, B: Chemical*, vol. 64, no. 1–3, p. 193–197, 2000.
- [18] C. Wang, X. Cheng, X. Zhou, P. Sun, X. Hu, K. Shimanoe, G. Lu, and N. Yamazoe, "Hierarchical α -fe2o3/nio composites with a hollow structure for a gas sensor," *ACS Applied Materials and Interfaces*, vol. 6, no. 15, p. 12031–12037, 2014.
- [19] T. Seiyama, A. Kato, K. Fujiishi, and M. Nagatani, "A new detector for gaseous components using semiconductive thin films," *Analytical Chemistry*, vol. 34, no. 11, p. 1502–1503, 1962.
- [20] P. J. Shaver, "Activated tungsten oxide gas detectors," *Applied Physics Letters*, vol. 11, no. 8, pp. 255–257, 1967.
- [21] Z. W. Pan, Z. R. Dai, and Z. L. Wang, "Nanobelts of semiconducting oxides," *Science*, vol. 291, no. 5510, p. 1947–1949, 2001.
- [22] E. Comini, G. Faglia, and G. Sberveglieri, "Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts," *Appl. Phys. Lett.*, vol. 81, p. 1869, 2002.
- [23] P. I. Gouma, "Nanostructured polymorphic oxides for advanced chemosensors nanostructured polymorphic oxides for advanced chemosensors," *Rev.Adv.Mater.Sci*, vol. 5, p. 147–154, 2003.
- [24] D. Sun, C. Chang, S. Li, and L. Lin, "Near-field electrospinning," *Nano Letters*, vol. 6, no. 4, pp. 839–842, 2006.
- [25] O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, E. C. Dickey, and C. A. Grimes, "Extreme changes in the electrical resistance of titania nanotubes with hydrogen exposure," *Advanced Materials*, vol. 15, no. 7-8, pp. 624–627, 2003.
- [26] Q. Wan, Q. H. Li, and Y. J. Chen, "Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts," *Appl. Phys. Lett.*, vol. 84, p. 3654, 2004.
- [27] S. v. Kalinin, J. Shin, and S. Jesse, "Electronic transport imaging in a multiwire chemical field-effect transistor device," *J. Appl. Phys.*, vol. 98, p. 44503, 2005.
- [28] M. Law, H. Kind, B. Messer, F. Kim, and P. Yang, "Photochemical sensing of no 2 with sno 2 nanoribbon nanosensors at room temperature**," *Angew. Chem. Int. Ed*, vol. 41, no. 13, 2002.
- [29] E. S. Snow, J. P. Novak, M. D. Lay, and F. K. Perkins, "1/f noise in single-walled carbon nanotube devices," *Applied Physics Letters*, vol. 85, no. 18, p. 4172–4174, 2004.
- [30] A. Rothschild and H. L. Tuller, "Gas sensors: New materials and processing approaches," *Journal of Electroceramics*, vol. 17, no. 2-4, pp. 1005–1012, 2006.
- [31] A. Kolmakov, D. O. Klenov, Y. Lilach, S. Stemmer, and M. Moskovitst, "Enhanced gas sensing by individual SnO 2 nanowires and nanobelts functionalized with Pd catalyst particles," *Nano Letters*, vol. 5, no. 4, pp. 667–673, 2005.
- [32] R. J. Wu, D. J. Lin, M. R. Yu, M. H. Chen, and H. F. Lai, "Ag@SnO2 core-shell material for use in fast-response ethanol sensor at room operating temperature," *Sensors and Actuators, B: Chemical*, vol. 178, pp. 185–191, 2013.
- [33] S. Si, C. Li, X. Wang, Q. Peng, and Y. Li, "Fe2o3/zno core-shell nanorods for gas sensors," *Sensors and Actuators B: Chemical*, vol. 119, no. 1, p. 52–56, 2006.
- [34] S. J. Kim, I. S. Hwang, J. K. Choi, Y. C. Kang, and J. H. Lee, "Enhanced c2h5oh sensing characteristics of nano-porous in2o3 hollow spheres prepared by sucrose-mediated hydrothermal reaction," *Sensors and Actuators B: Chemical*, vol. 155, no. 2, p. 512–518, 2011.
- [35] F. Gyger, M. H€, C. Feldmann, N. Barsan, and U. Weimar, "Nanoscale sno 2 hollow spheres and their application as a gas-sensing material," *Chem. Mater*, vol. 22, p. 4821, 2010.
- [36] L. Li, H. Song, and X. Chen, "Hollow carbon microspheres prepared from polystyrene microbeads," *Carbon*, vol. 44, no. 3, p. 596–599, 2006.

- [37] Z. Zhong, Y. Yin, B. Gates, and Y. Xia, "Preparation of mesoscale hollow spheres of TiO_2 and SnO_2 by templating against crystalline arrays of polystyrene beads," *Advanced Materials*, vol. 12, no. 3, p. 206–209, 2000.
- [38] F. Caruso, R. A. Caruso, and H. Möhwald, "Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating," *Science*, vol. 282, no. 5391, p. 1111–1114, 1998.
- [39] X. W. Lou, L. A. Archer, and Z. Yang, "Hollow micro-/nanostructures: Synthesis and applications," *Advanced Materials*, vol. 20, no. 21, p. 3987–4019, 2008.
- [40] Z. Li, Q. Zhao, W. Fan, and J. Zhan, "Porous SnO_2 nanospheres as sensitive gas sensors for volatile organic compounds detection," *Nanoscale*, vol. 3, no. 4, p. 1646–1652, 2011.
- [41] G. R. Bourret and R. B. Lennox, "1d $\text{Cu}(\text{OH})_2$ nanomaterial synthesis templated in water microdroplets," *Journal of the American Chemical Society*, vol. 132, no. 19, p. 6657–6659, 2010.
- [42] C. I. Zoldesi and A. Imhof, "Synthesis of monodisperse colloidal spheres, capsules, and microballoons by emulsion templating," *Advanced Materials*, vol. 17, no. 7, p. 924–928, 2005.
- [43] S. J. Kim, I. S. Hwang, C. W. Na, I. D. Kim, Y. C. Kang, and J. H. Lee, "Ultrasensitive and selective $\text{C}_2\text{H}_5\text{OH}$ sensors using rh-loaded In_2O_3 hollow spheres," *Journal of Materials Chemistry*, vol. 21, no. 46, p. 18560–18567, 2011.
- [44] X. Wen Lou, C. Yuan, L. A. Archer, W. Lou, C. Yuan, and L. A. Archer, "Colloid synthesis shell-by-shell synthesis of tin oxide hollow colloids with nanoarchitected walls: Cavity size tuning and functionalization**," *Small*, vol. 3, no. 2, p. 261–265, 2007.
- [45] Y. Zhu, T. Ikoma, N. Hanagata, and S. Kaskel, "Rattle-type $\text{Fe}_3\text{O}_4@\text{SiO}_2$ hollow mesoporous spheres as carriers for drug delivery," *Small*, vol. 6, no. 3, pp. 471–478, 2010.
- [46] J. Liu, W. Li, and A. Manthiram, "Dense core-shell structured SnO_2/C composites as high performance anodes for lithium ion batteries," *Chemical Communications*, vol. 46, no. 9, pp. 1437–1439, 2010.
- [47] L. Wang, H. Dou, Z. Lou, and T. Zhang, "Encapsulated nanoreactors ($\text{Au}@\text{SnO}_2$): A new sensing material for chemical sensors," *Nanoscale*, vol. 5, no. 7, p. 2686–2691, 2013.
- [48] N. Murata, T. Suzuki, M. Kobayashi, F. Togoh, and K. Asakura, "Characterisation of Pt-doped SnO_2 catalyst for a high-performance micro gas sensor," *Phys. Chem. Chem. Phys*, vol. 15, p. 17938, 2013.
- [49] T. Suzuki, S. Soma, and T. Nagase, "Methane Sensor for Cordless Utility Gas Alarms," *Fuji Electric Review*, vol. 84, no. 4, pp. 278–282, 2012.
- [50] A. Venugopal, A. Pirkle, R. M. Wallace, L. Colombo, and E. M. Vogel, "Contact resistance studies of metal on HOPG and graphene stacks," *AIP Conference Proceedings*, vol. 1173, pp. 324–327, 2009.
- [51] K. Nagashio, T. Nishimura, K. Kita, and A. Toriumi, "Contact resistivity and current flow path at metal/graphene contact," *Applied Physics Letters*, vol. 97, no. 14, pp. 2012–2015, 2010.
- [52] Y. Sui and J. Appenzeller, "Screening and interlayer coupling in multilayer graphene field-effect transistors," *Nano Letters*, vol. 9, no. 8, pp. 2973–2977, 2009.
- [53] K. Nagashio and A. Toriumi, "Density-of-states limited contact resistance in graphene field-effect transistors," *Japanese Journal of Applied Physics*, vol. 50, no. 7 PART 1, 2011.
- [54] J. S. Moon, M. Antcliffe, H. C. Seo, D. Curtis, S. Lin, A. Schmitz, I. Milosavljevic, A. A. Kiselev, R. S. Ross, D. K. Gaskill, P. M. Campbell, R. C. Fitch, K. M. Lee, and P. Asbeck, "Ultra-low resistance ohmic contacts in graphene field effect transistors," *Applied Physics Letters*, vol. 100, no. 20, 2012.
- [55] C. Gong, G. Lee, B. Shan, E. M. Vogel, R. M. Wallace, and K. Cho, "First-principles study of metal-graphene interfaces," *Journal of Applied Physics*, vol. 108, no. 12, 2010.
- [56] X. Ji, Y. Wang, and Z. Yu, "First-principle investigation of Ti wetting layer influence on metal-graphene contact," *International Conference on Simulation of Semiconductor Processes and Devices, SISPAD*, pp. 392–395, 2013.

- [57] P. A. Khomyakov, G. Giovannetti, P. C. Rusu, G. Brocks, J. Van Den Brink, and P. J. Kelly, "First-principles study of the interaction and charge transfer between graphene and metals," *Physical Review B - Condensed Matter and Materials Physics*, vol. 79, no. 19, pp. 1–12, 2009.
- [58] K. T. Chan, J. B. Neaton, and M. L. Cohen, "First-principles study of metal adatom adsorption on graphene," *Physical Review B - Condensed Matter and Materials Physics*, vol. 77, no. 23, pp. 1–12, 2008.
- [59] M. García-Mota, D. J. Oroya, E. Artacho, X. Cartoixa, and J. J. Palacios, "Integration of graphene into nanoelectronic devices: Insights from atomistic simulations," *Advanced Materials - TechConnect Briefs 2016*, vol. 1, pp. 53–56, 2016.
- [60] K. Nagashio, T. Yamashita, J. Fujita, T. Nishimura, K. Kita, and A. Toriumi, "Impacts of graphene/SiO₂ interaction on FET mobility and Raman spectra in mechanically exfoliated graphene films," *Technical Digest - International Electron Devices Meeting, IEDM*, pp. 564–567, 2010.
- [61] T. Mueller, F. Xia, M. Freitag, J. Tsang, and P. Avouris, "Role of contacts in graphene transistors: A scanning photocurrent study," *Physical Review B - Condensed Matter and Materials Physics*, vol. 79, no. 24, pp. 1–6, 2009.
- [62] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, and J. M. Tour, "Laser-induced porous graphene films from commercial polymers," *Nature Communications*, vol. 5, p. 5714, dec 2014.
- [63] F. Xia, V. Perebeinos, Y. M. Lin, Y. Wu, and P. Avouris, "The origins and limits of metal-graphene junction resistance," *Nature Nanotechnology*, vol. 6, no. 3, pp. 179–184, 2011.
- [64] F. A. Chaves, D. Jiménez, A. A. Sagade, W. Kim, J. Riikonen, H. Lipsanen, and D. Neumaier, "A physics-based model of gate-tunable metal-graphene contact resistance benchmarked against experimental data," *2D Materials*, vol. 2, no. 2, pp. 1–8, 2015.
- [65] B. Kretz, C. S. Pedersen, D. Stradi, M. Brandbyge, and A. Garcia-Lekue, "Atomistic Insight into the Formation of Metal-Graphene One-Dimensional Contacts," *Physical Review Applied*, vol. 10, no. 2, p. 1, 2018.
- [66] T. Cusati, G. Fiori, A. Gahoi, V. Passi, M. C. Lemme, A. Fortunelli, and G. Iannaccone, "Electrical properties of graphene-metal contacts," *Scientific Reports*, vol. 7, no. 1, pp. 1–11, 2017.
- [67] F. Driussi, S. Venica, A. Gahoi, A. Gambi, P. Giannozzi, S. Kataria, M. C. Lemme, P. Palestri, and D. Esseni, "Improved understanding of metal-graphene contacts," *Microelectronic Engineering*, vol. 216, no. June, p. 111035, 2019.
- [68] M. König, G. Ruhl, A. Gahoi, S. Wittmann, T. Preis, J. M. Batke, I. Costina, and M. C. Lemme, "Accurate Graphene-Metal Junction Characterization," *IEEE Journal of the Electron Devices Society*, vol. 7, no. c, pp. 227–238, 2019.
- [69] C. Yang, Z. Wang, Y. Jia, P. Peng, X. Gong, L. Ren, and Y. Fu, "Contact resistance between graphene and metal," *China Semiconductor Technology International Conference 2016, CSTIC 2016*, pp. 1–3, 2016.
- [70] W. Liu, J. Wei, X. Sun, and H. Yu, "A study on graphene-metal contact," *Crystals*, vol. 3, no. 1, pp. 257–274, 2013.
- [71] C. Liang, Y. Wang, and T. Li, "Studies on contact resistance in graphene based devices," *Microsystem Technologies*, vol. 22, no. 8, pp. 1943–1947, 2015.
- [72] F. Léonard and A. A. Talin, "Electrical contacts to one- and two-dimensional nanomaterials," *Nature Nanotechnology*, vol. 6, no. 12, pp. 773–783, 2011.
- [73] H. Murrmann and D. Widmann, "Current Crowding on Metal Contacts to Planar Devices," *IEEE Transactions on Electron Devices*, vol. 16, no. 12, pp. 1022–1024, 1969.
- [74] P. Zhang, Y. Y. Lau, and R. M. Gilgenbach, "Analysis of current crowding in thin film contacts from exact field solution," *Journal of Physics D: Applied Physics*, vol. 48, no. 47, p. 475501, 2015.
- [75] J. H. Klootwijk and C. E. Timmering, "Merits and limitations of circular TLM structures for contact resistance determination for novel III-V HBTs," *IEEE International Conference on Microelectronic Test Structures*, vol. 17, no. March, pp. 247–252, 2004.

- [76] R. Zan, U. Bangert, Q. Ramasse, and K. S. Novoselov, "Interaction of metals with suspended graphene observed by transmission electron microscopy," *Journal of Physical Chemistry Letters*, vol. 3, no. 7, pp. 953–958, 2012.
- [77] S. Wang, D. Mao, A. Muhammad, S. Peng, D. Zhang, J. Shi, and Z. Jin, "Characterization of the quality of metal–graphene contact with contact end resistance measurement," *Applied Physics A: Materials Science and Processing*, vol. 122, no. 7, 2016.
- [78] A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel, R. S. Ruoff, and R. M. Wallace, "The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO₂," *Applied Physics Letters*, vol. 99, no. 12, pp. 2011–2014, 2011.
- [79] C. A. Chavarin, A. A. Sagade, D. Neumaier, G. Bacher, and W. Mertin, "On the origin of contact resistances in graphene devices fabricated by optical lithography," *Applied Physics A: Materials Science and Processing*, vol. 122, no. 2, pp. 1–5, 2016.
- [80] W. Li, C. A. Hacker, G. Cheng, Y. Liang, B. Tian, A. R. Hight Walker, C. A. Richter, D. J. Gundlach, X. Liang, and L. Peng, "Highly reproducible and reliable metal/graphene contact by ultraviolet-ozone treatment," *Journal of Applied Physics*, vol. 115, no. 11, 2014.
- [81] A. Meersha, H. B. Variar, K. Bhardwaj, A. Mishra, S. Raghavan, N. Bhat, and M. Shrivastava, "Record low metal - (CVD) graphene contact resistance using atomic orbital overlap engineering," *Technical Digest - International Electron Devices Meeting, IEDM*, no. Cvd, pp. 5.3.1–5.3.4, 2017.
- [82] A. Nath, M. Currie, A. K. Boyd, V. D. Wheeler, A. D. Koehler, M. J. Tadjer, Z. R. Robinson, K. Sridhara, S. C. Hernandez, J. A. Wollmershauser, J. T. Robinson, R. L. Myers-Ward, M. V. Rao, and D. K. Gaskill, "In search of quantum-limited contact resistance: Understanding the intrinsic and extrinsic effects on the graphene-metal interface," *2D Materials*, vol. 3, no. 2, pp. 1–13, 2016.
- [83] Z. Z. He, K. W. Yang, C. Yu, J. Li, Q. B. Liu, W. L. Lu, Z. H. Feng, and S. J. Cai, "Improvement of Metal-Graphene Ohmic Contact Resistance in Bilayer Epitaxial Graphene Devices," *Chinese Physics Letters*, vol. 32, no. 11, 2015.
- [84] K. Keramatnejad, Y. S. Zhou, D. W. Li, H. R. Golgir, X. Huang, Q. M. Zhou, J. F. Song, S. Ducharme, and Y. F. Lu, "Laser-Assisted Nanowelding of Graphene to Metals: An Optical Approach toward Ultralow Contact Resistance," *Advanced Materials Interfaces*, vol. 4, no. 15, pp. 1–7, 2017.
- [85] H. Y. Park, W. S. Jung, D. H. Kang, J. Jeon, G. Yoo, Y. Park, J. Lee, Y. H. Jang, J. Lee, S. Park, H. Y. Yu, B. Shin, S. Lee, and J. H. Park, "Extremely Low Contact Resistance on Graphene through n-Type Doping and Edge Contact Design," *Advanced Materials*, vol. 28, no. 5, pp. 864–870, 2016.
- [86] K. Y. Huang, A. S. Chou, S. Y. Liu, W. Y. Cheng, C. L. Hung, C. S. Li, M. S. Ho, and C. I. Wu, "Ultralow-contact-resistance graphene field-effect transistors fabricated with P-type solution doping," *Applied Physics Express*, vol. 11, no. 7, 2018.
- [87] W. Zhang, C. T. Lin, K. K. Liu, T. Tite, C. Y. Su, C. H. Chang, Y. H. Lee, C. W. Chu, K. H. Wei, J. L. Kuo, and L. J. Li, "Opening an electrical band gap of bilayer graphene with molecular doping," *ACS Nano*, vol. 5, no. 9, pp. 7517–7524, 2011.
- [88] B. Huard, N. Stander, J. A. Sulpizio, and D. Goldhaber-Gordon, "Evidence of the role of contacts on the observed electron-hole asymmetry in graphene," *Physical Review B - Condensed Matter and Materials Physics*, vol. 78, no. 12, 2008.
- [89] J. W. Suk, W. H. Lee, J. Lee, H. Chou, R. D. Piner, Y. Hao, D. Akinwande, and R. S. Ruoff, "Enhancement of the electrical properties of graphene grown by chemical vapor deposition via controlling the effects of polymer residue," *Nano Letters*, vol. 13, no. 4, pp. 1462–1467, 2013.
- [90] W. Li, Y. Liang, D. Yu, L. Peng, K. P. Pernstich, T. Shen, A. R. Hight Walker, G. Cheng, C. A. Hacker, C. A. Richter, Q. Li, D. J. Gundlach, and X. Liang, "Ultraviolet/ozone treatment to reduce metal-graphene contact resistance," *Applied Physics Letters*, vol. 102, no. 18, 2013.

- [91] C. Gong, H. C. Floresca, D. Hinojos, S. McDonnell, X. Qin, Y. Hao, S. Jandhyala, G. Mordi, J. Kim, L. Colombo, R. S. Ruoff, M. J. Kim, K. Cho, R. M. Wallace, and Y. J. Chabal, "Rapid selective etching of PMMA residues from transferred graphene by carbon dioxide," *Journal of Physical Chemistry C*, vol. 117, no. 44, pp. 23000–23008, 2013.
- [92] Y. Jia, X. Gong, P. Peng, Z. Wang, Z. Tian, L. Ren, Y. Fu, and H. Zhang, "Toward High Carrier Mobility and Low Contact Resistance: Laser Cleaning of PMMA Residues on Graphene Surfaces," *Nano-Micro Letters*, vol. 8, no. 4, pp. 336–346, 2016.
- [93] S. Gahng, C. H. Ra, Y. J. Cho, J. A. Kim, T. Kim, and W. J. Yoo, "Reduction of metal contact resistance of graphene devices via CO₂ cluster cleaning," *Applied Physics Letters*, vol. 104, no. 22, 2014.
- [94] M. S. Choi, S. H. Lee, and W. J. Yoo, "Plasma treatments to improve metal contacts in graphene field effect transistor," *Journal of Applied Physics*, vol. 110, no. 7, 2011.
- [95] W. S. Leong, H. Gong, and J. T. Thong, "Low-contact-resistance graphene devices with nickel-etched-graphene contacts," *ACS Nano*, vol. 8, no. 1, pp. 994–1001, 2014.
- [96] S. Z. Yu, Y. Song, J. R. Dong, Y. R. Sun, Y. M. Zhao, and Y. He, "Low specific contact resistivity to graphene achieved by AuGe/Ni/Au and annealing process," *Chinese Physics B*, vol. 25, no. 11, 2016.
- [97] H. Ramamoorthy and R. Somphonsane, "In-situ current annealing of graphene-metal contacts," *Journal of Physics: Conference Series*, vol. 1144, no. 1, 2018.
- [98] Y. Zhang and X. P. Qu, "Improved contact resistivity and enhanced mobility of metal-graphene FET by inserting ultra-thin MoO_x layer at source/drain region," *AIP Advances*, vol. 9, no. 5, 2019.
- [99] J. Moser, A. Barreiro, and A. Bachtold, "Current-induced cleaning of graphene," *Applied Physics Letters*, vol. 91, no. 16, pp. 1–4, 2007.
- [100] D. C. Mao, Z. Jin, S. Q. Wang, D. Y. Zhang, J. Y. Shi, S. A. Peng, and X. Y. Wang, "Depositing aluminum as sacrificial metal to reduce metal-graphene contact resistance," *Chinese Physics B*, vol. 25, no. 7, 2016.
- [101] A. Hsu, H. Wang, K. K. Kim, J. Kong, and T. Palacios, "Impact of graphene interface quality on contact resistance and RF device performance," *IEEE Electron Device Letters*, vol. 32, no. 8, pp. 1008–1010, 2011.
- [102] J. Lee, Y. Kim, H. J. Shin, C. Lee, D. Lee, C. Y. Moon, J. Lim, and S. Chan Jun, "Clean transfer of graphene and its effect on contact resistance," *Applied Physics Letters*, vol. 103, no. 10, 2013.
- [103] E. J. Lee, K. Balasubramanian, R. T. Weitz, M. Burghard, and K. Kern, "Contact and edge effects in graphene devices," *Nature Nanotechnology*, vol. 3, no. 8, pp. 486–490, 2008.
- [104] H. Pandey, M. Shaygan, S. Sawallich, S. Kataria, Z. Wang, A. Noculak, M. Otto, M. Nagel, R. Negra, D. Neumaier, and M. C. Lemme, "All CVD Boron Nitride Encapsulated Graphene FETs with CMOS Compatible Metal Edge Contacts," *IEEE Transactions on Electron Devices*, vol. 65, no. 10, pp. 4129–4134, 2018.
- [105] B. Krishna Bharadwaj, D. Nath, R. Pratap, and S. Raghavan, "Making consistent contacts to graphene: Effect of architecture and growth induced defects," *Nanotechnology*, vol. 27, no. 20, pp. 1–6, 2016.
- [106] A. D. Franklin, S. J. Han, A. A. Bol, and V. Perebeinos, "Double contacts for improved performance of graphene transistors," *IEEE Electron Device Letters*, vol. 33, no. 1, pp. 17–19, 2012.
- [107] X. Ji, Y. Wang, and Z. Yu, "A first-principle investigation of double-side CVD catalyst metal/graphene contacts," *Physical Chemistry Chemical Physics*, vol. 16, no. 24, pp. 12327–12331, 2014.
- [108] L. Adamska, Y. Lin, A. J. Ross, M. Batzill, and I. I. Oleynik, "Atomic and electronic structure of simple metal/graphene and complex metal/graphene/metal interfaces," *Physical Review B - Condensed Matter and Materials Physics*, vol. 85, no. 19, pp. 1–8, 2012.
- [109] T. Chu and Z. Chen, "Understanding the electrical impact of edge contacts in few-layer graphene," *ACS Nano*, vol. 8, no. 4, pp. 3584–3589, 2014.
- [110] Y. Matsuda, W. Q. Deng, and W. A. Goddard, "Contact resistance for "end-contacted" metal-graphene and metal-nanotube interfaces from quantum mechanics," *Journal of Physical Chemistry C*, vol. 114, no. 41, pp. 17845–17850, 2010.

- [111] D. W. Yue, C. H. Ra, X. C. Liu, D. Y. Lee, and W. J. Yoo, "Edge contacts of graphene formed by using a controlled plasma treatment," *Nanoscale*, vol. 7, no. 2, pp. 825–831, 2015.
- [112] J. T. Smith, A. D. Franklin, D. B. Farmer, and C. D. Dimitrakopoulos, "Reducing contact resistance in graphene devices through contact area patterning," *ACS Nano*, vol. 7, no. 4, pp. 3661–3667, 2013.
- [113] R. Wang, J. Wang, H. Gong, Z. Luo, D. Zhan, Z. Shen, and J. T. Thong, "Cobalt-mediated crystallographic etching of graphite from defects," *Small*, vol. 8, no. 16, pp. 2515–2523, 2012.
- [114] S. Min Song, T. Yong Kim, O. Jae Sul, W. Cheol Shin, and B. Jin Cho, "Improvement of graphene-metal contact resistance by introducing edge contacts at graphene under metal," *Applied Physics Letters*, vol. 104, no. 18, pp. 2012–2015, 2014.
- [115] V. Passi, A. Gahoi, J. Ruhkopf, S. Kataria, F. Vaurette, E. Pallecchi, H. Happy, and M. C. Lemme, "Contact resistance Study of 'edge-contacted' metal-graphene interfaces," *European Solid-State Device Research Conference*, vol. 2016-Octob, pp. 236–239, 2016.
- [116] V. Passi, A. Gahoi, E. G. Marin, T. Cusati, A. Fortunelli, G. Iannaccone, G. Fiori, and M. C. Lemme, "Ultralow Specific Contact Resistivity in Metal–Graphene Junctions via Contact Engineering," *Advanced Materials Interfaces*, vol. 6, no. 1, pp. 1–8, 2019.
- [117] A. C. Ferrari and D. M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of graphene," *Nature Nanotechnology*, vol. 8, no. 4, p. 235–246, 2013.
- [118] V. N. Kotov, B. Uchoa, V. M. Pereira, F. Guinea, and A. H. Castro Neto, "Electron-Electron Interactions in Graphene: Current Status and Perspectives," *Reviews of Modern Physics*, vol. 84, pp. 1067–1125, jul 2012.
- [119] M. Lazzeri, C. Attaccalite, L. Wirtz, and F. Mauri, "Impact of the electron-electron correlation on phonon dispersion: Failure of LDA and GGA DFT functionals in graphene and graphite," *Physical Review B - Condensed Matter and Materials Physics*, vol. 78, no. 8, pp. 8–11, 2008.
- [120] J.-B. Wu, M.-L. Lin, X. Cong, H.-N. Liu, and P.-H. Tan, "Raman spectroscopy of graphene-based materials and its applications in related devices," *Chemical Society Reviews*, vol. 47, pp. 1822–1873, mar 2018.
- [121] S. Piscanec, M. Lazzeri, A. C. Ferrari, F. Mauri, and J. Robertson, "Kohn anomalies in graphite and nanotubes," tech. rep., 2004.
- [122] L. M. Malard, M. A. Pimenta, G. Dresselhaus, and M. S. Dresselhaus, "Raman spectroscopy in graphene," *Physics Reports*, vol. 473, pp. 51–87, apr 2009.