

Title	Monolayer doping of Si with improved oxidation resistance
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Publication date	2016-01-26
Original Citation	O'CONNELL, J., COLLINS, G., MCGLACKEN, G. P., DUFFY, R. & HOLMES, J. D. 2016. Monolayer Doping of Si with Improved Oxidation Resistance. ACS Applied Materials & Interfaces, 8, 4101-4108. http://dx.doi.org/10.1021/acsami.5b11731
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://pubs.acs.org/journal/aamick - 10.1021/acsami.5b11731
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Download date	2025-06-29 03:54:33
Item downloaded from	https://hdl.handle.net/10468/2465



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Monolayer doping of Si with improved oxidation resistance

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Keywords: Monolayer, doping, alkyne-azide cycloaddition, phosphorus, click chemistry, arsenic, silicon, functionalization

Abstract

In this article, the functionalization of planar silicon with arsenic- and phosphorus-based azides was investigated. Covalently bonded and well-ordered alkyne-terminated monolayers were prepared from a range of commercially available dialkyne precursors using a well-known thermal hydrosilylation mechanism to form an acetylene-terminated monolayer. The terminal acetylene moieties were further functionalized through the application of copper-catalysed azide-alkyne cycloaddition (CuAAC) reactions between dopant-containing azides and the terminal acetylene groups. The introduction of dopant molecules *via* this method does not require harsh conditions typically employed in traditional monolayer doping approaches, enabling greater surface coverage with improved resistance towards re-oxidation. X-ray photoelectron spectroscopy studies showed successful dialkyne incorporation with minimal Si surface oxidation and also showed successful azide-alkyne cycloaddition through monitoring of the C *1s* and N *1s* core-level spectra. Electrochemical capacitance-voltage measurements showed effective diffusion of the activated dopant atoms into the Si substrates.

Introduction

A growing challenge for the semiconductor and microelectronics industry is the ability to effectively dope nanoscale materials positioned in non-planar and small feature size device geometries.¹ New methodologies for shallow doping of semiconductors are required if complementary metal oxide semiconductor (CMOS) devices are to continue scaling in accordance with Moore's Law.^{2,3} Ion beam implantation, the highly energetic process of bombarding a semiconductor surface with ions has been the conventional method of doping for a number of years but its efficacy is much reduced at the nanoscale.⁴ Numerous problems, such as

the inability to control the abruptness of the profile over a nanometre range, the crystallographic damage caused to the surface and the incompatibility of the technique with quasi-one dimensional structures such as nanowires, must be overcome if device geometries are to continue to scale effectively. Many potential alternatives to ion beam implantation have been proposed ranging from plasma immersion ion implantation,^{5,6} polymeric spin-on dopants^{7,8} and monolayer doping (MLD).^{7,9–14} The traditional monolayer doping process combines the rich surface chemistry of semiconductors with the self-assembly of dopant containing molecules on the semiconductor surface, most commonly *via* a one-step hydrosilylation process. MLD has already been shown to be a suitable technique for shallow doping of Si devices with complex and non-planar geometries, allowing fine control over dopant profiles. The functionalization of Si surfaces can also improve the resistance of the surfaces towards oxidation, a requirement for sensor applications^{15–23}

This article describes the use of copper-catalysed alkyne-azide cycloaddition (CuAAC) reactions between a primary passivation layer on a Si surface composed of di-alkynes with reactive terminal alkyne moieties, and a dopant-containing azide. A schematic showing the general functionalization method is shown in **Figure 1**. Firstly, di-alkynes of increasing lengths (between 7 and 10 carbons) were attached to the Si-H surface using a thermal hydrosilylation method.^{24,25} The dopant-containing azide was then “clicked” onto the alkyne moiety using a Huisgen 1,3-dipolar cycloaddition reaction under very mild conditions, allowing the formation of tightly packed, high-quality monolayers on Si surfaces. Using a commercially-available di-alkyne is advantageous as it is not necessary to synthesise the required di-alkyne. Additionally, the symmetrical structure of the dialkyne molecule permits the acetylene-terminated monolayer

to be formed in one quick step. The Huisgen 1,3-dipolar cycloaddition reaction is one of many reactions independently specified as a “click” reaction by Sharpless *et al.* and also by Meldal.^{26,27} Click reactions are nominally of wide scope, selective, proceed in good yield and are exceptionally hardy to most reaction factors considered harsh, such as the presence of oxygen, aqueous solvents and high temperatures.²⁸ The hydrosilylation reaction remains the most widely used method to produce well-ordered alkyl molecular layers on Si but some disadvantages still remain.²⁹ For example, the high temperatures required for hydrosilylation limits the type of dopant molecules that can be used in MLD to those which are stable at the reaction temperature. Additionally the presence of any trace amounts of water or oxygen, combined with a high-temperature reaction can cause re-growth of surface oxides, which can disrupt the dopant-containing monolayer. Whilst click chemistry functionalization has been used in materials science for a range of applications such as redox behaviour studies and protein adsorption^{30–33}, to the best of our knowledge the technique has not been used for MLD of semiconductors. The coupling of azides to terminal alkynes is one of the most useful modular approaches to building-up monolayers. The click-chemistry approach described in this article greatly suppresses the effect that ambient, aerobic conditions could potentially have on the underlying Si surface due to the protection that the primary di-alkyne passivation layer offers. Additionally, the dopant-containing azides used in this study are resistant to attack by atmospheric oxygen and moisture. The conventional MLD approach typically involves the use or design of a molecular precursor that contains not only the dopant atom but also the unsaturated C=C bonds required for the hydrosilylation reaction to take place between the C=C labile site and H-terminated surface. While this route is experimentally convenient for the substrate functionalization step, these types of precursors are typically air-sensitive with complex synthesis procedures and difficult to

purify. Additionally, the molecular footprints of the molecule, as well as steric effects from substituents, may affect packing at the substrate surface potentially causing pinhole oxidation points. The method described in this article separates the C=C labile site from the dopant molecule and instead, introduces the dopant molecule *via* the subsequent alkyne-azide cycloaddition reaction. This two-step process allows the use of established hydrosilylation chemistry with commercially available and decomposition-resistant molecules to form well-ordered monolayers, which offer much improved oxidation protection for the underlying substrate. The terminal acetylene groups act as reactive “handles” on which the dopant-containing molecules can be “clicked” using relatively mild reaction conditions and green solvents.

Experimental

Ascorbic acid, copper sulphate, sodium borohydride, arsenic trichloride, 1,6-heptadiyne, 1,7-octadiyne and 1,9-octadiyne were purchased from Acros Organics. 1,8-octadiyne, carbon tetrachloride, sodium azide and diphenylphosphoryl azide (DPPA) were purchased from Sigma Aldrich. All alkynes were pre-dried using sodium borohydride and distilled under reduced pressure before use. Mesitylene and dimethylformamide (DMF) were dried and distilled from calcium hydride and stored over molecular sieves before use. All other chemicals were used as received without further purification. Monocrystalline <100> silicon, undoped, was obtained from University Wafer, Boston, Massachusetts. All chemical manipulations were carried out under strict inert conditions in an atmosphere of ultra-high purity argon from Air Products Inc. using a combination of Schlenk apparatus and an Innovative Technologies inert-atmosphere glovebox. X-ray photoelectron spectroscopy (XPS) spectra were acquired on an Oxford Applied

Research Escabase XPS system equipped with a CLASS VM 100 mm mean radius hemispherical electron energy analyzer with a triple-channel detector arrangement in an analysis chamber with a base pressure of 5.0×10^{-10} mbar. Survey scans were acquired between 0-1400 eV with a step size of 0.7 eV, a dwell time of 0.5 s and a pass energy of 100 eV. Core level scans were acquired at the applicable binding energy range with a step size of 0.1 eV, dwell time of 0.5 s and pass energy of 20 eV averaged over 50 scans. A non-monochromated Al- $K\alpha$ X-ray source at 200 W power was used for all scans. The N 1s spectra for each sample were acquired immediately after the survey spectrum to negate any effect of the X-ray induced bremsstrahlung on the azo- groups on the surface. All spectra were acquired at a take-off angle of 90° with respect to the analyzer axis and were charge corrected with respect to the C 1s photoelectric line by rigidly shifting the binding energy scale to 285 eV. Data were processed using CasaXPS software where a Shirley background correction was employed and peaks were fitted to Voigt profiles. To ensure accurate quantification, atomic sensitivity factors were taken from the instrument spectrum acquisition software and manually inputted into the data processing software.

Synthesis of arsenic azide (AsN_3)₃

Arsenic azide (AA) (AsN_3)₃ was prepared using literature procedures from Klapökte *et al.* CAUTION: While (AsN_3)₃ is explosive and can explode on contact with a metal syringe or spatula it may be handled safely in solution. Briefly, sodium azide (NaN_3) (10 g, 150 mmol) was dissolved in a minimum amount of water to make up a saturated solution and was activated by the addition of hydrazine hydrate (1 mol. %) and left to stir for 12 h. Acetone was added to precipitate the activated NaN_3 . The precipitate was filtered and washed copiously with acetone

and ethanol. 1.06 g (10 mmol) of the activated NaN_3 was added to a two-necked round bottom flask and suspended in 10 ml of carbon tetrachloride (CCl_4). To this solution was added 0.3 mL of arsenic trichloride (AsCl_3) and the solution was stirred vigorously for 12 h to ensure complete mixing of the reagents. The suspension was then filtered to remove unreacted NaN_3 and the NaCl side product and the yellow, oily, filtrate in CCl_4 was stored under Ar before being used directly for the CuAAC reactions. A reaction scheme is shown in **Scheme S1** in Supporting Information.

General procedure for Si substrate functionalization with di-alkynes.

All glassware was cleaned with Alconox detergent followed by copious rinsing with water and then cleaned with a piranha wash (CAUTION: this is a strong oxidizing agent and reacts violently with organic substances), dried in an oven overnight at 130 °C and allowed to cool under a stream of dry Ar on a Schlenk line. 1,7-octadiyne was dissolved in previously dried mesitylene (5 ml) to make up a 25 % v/v solution. The solution was degassed and dried using several freeze-pump-thaw cycles and left to purge under a positive pressure of argon while the substrate was being prepared. A 1.5 cm² sample of Si was degreased, cleaned by standard RCA washes³⁴ of a 5:1:1 solution of H_2O , NH_4OH and H_2O_2 followed by a 5:1:1 solution of H_2O , HCl and H_2O_2 . Following a rinse in H_2O the substrate was immersed in a 2.5 % solution of hydrofluoric acid for 1.5 min to remove surface oxides and to induce H-passivation of the surface. These etching parameters are known to give a mainly di-hydride terminated surface.³⁵ The substrate was dried under a stream of dry nitrogen and placed immediately into a two neck round bottom flask under argon to prevent re-oxidation of the surface. The dialkyne solution was cannulated under a positive pressure of Ar into the flask containing the H-passivated Si

substrate. The flask was then heated to 170 °C under Ar and left for 2 h at reflux. After the reaction had completed the substrate was removed from the vessel and immediately immersed in a vial of anhydrous toluene and sonicated to remove any physisorbed species. The sample was rinsed in a vial of fresh anhydrous toluene and sonicated in successive vials of anhydrous toluene, dichloromethane, ethyl acetate, ethanol and hexane with careful drying in a N₂ stream between each vial. The sample was kept under an inert atmosphere before removal for the subsequent “click” reaction. This process was repeated for the remaining dialkynes.

General procedure for CuAAC “click” reaction

A sample previously functionalized with the applicable dialkyne was placed into a cleaned two-neck round bottom flask. To this flask was added: i) the applicable azide (10 mM in DMF), ii) copper(II) sulphate (0.8 mol% relative to the azide) and (iii) ascorbic acid (80 mol% relative to the azide). The flask was heated to a temperature of 60 °C and left for 12 h under Ar. The samples were rinsed with an excess of water and ethanol and rinsed with 0.5 M hydrochloric acid solution to remove any potential traces of physisorbed Cu salts. Samples were rinsed once more with ethanol and water immediately prior to analysis.

Carrier profiling

ECV profiling was carried out on a WEP Control CVP21 Wafer Profiler using 0.1 M ammonium hydrogen bifluoride as the etchant. Scanning parameters were automatically controlled by the instrument by selecting the appropriate sample type, layer map and etchant combination. The error in the active carrier concentration did not exceed 15 % for the measurements as determined by the instrument control software.

Results and Discussion

Click modification of the 1,7 octadiyne functionalized Si surface with diphenylphosphoryl azide (DPPA)

Figure 2(a) shows a Si $2p$ core level spectrum from a Si (100) surface after a standard RCA clean and fresh HF etch. The spectrum shows no evidence of Si oxides typically observed at binding energies between 101 and 104 eV and exhibits a primary peak centred at ~ 99 eV³⁶ implying the presence of a clean, pristine surface required for the functionalization steps. **Figure 2(b)** shows the Si $2p$ core level spectrum after functionalization with 1,7-octadiyne *via* thermally-induced hydrosilylation. The survey spectrum shown in **Figure S1(a)** (see Supporting Information) indicates the presence of Si, O and C which is consistent with the presence of an organic monolayer on the Si substrate.^{37–39} The absence of oxide associated peaks in the Si $2p$ core level spectrum suggest that a high-quality organic monolayer has formed which offers good resistance toward re-oxidation of the underlying substrate. A small O $1s$ peak at 532 eV can be attributed to contributions from adventitiously adsorbed H₂O from air during sample transport to the UHV environment of the XPS spectrometer. The C $1s$ core-level XPS spectrum of a 1,7-octadiyne functionalized Si substrate is shown in **Figure S1(b)**. A broad feature centred at ~ 285 eV that is consistent with chemical contributions from Si-C and C-C bonds can be observed. This 1,7-octadiyne functionalized Si surface was subsequently functionalized with the DPPA molecule *via* the copper-catalyzed azide-alkyne cycloaddition. **Figure S2(a)** shows an XPS survey scan of a DPPA functionalized Si sample showing the appearance of a N $1s$ signal at approximately 400 eV when compared to **Figure S1(a)**. The survey spectrum shown in **Figure S2(b)** shows a AA functionalized Si sample showing the presence of N $1s$ and As $2p$ signals at approximately 400 and 1325 eV respectively, which are absent from the di-alkyne functionalized

substrate shown in **Figure S1(a)**. **Figure 3(a)** shows a C *1s* core level spectrum for a substrate after attachment of the P-containing azide. Deconvolution of the C *1s* core level spectrum shows a peak at 285 eV attributed to the aliphatic primary passivation layer. A peak centred near 287 eV indicates the presence of a C-N moiety and tentative evidence for the formation of the [1,2,3]-triazole ring, which is characteristic of alkyne-azide cycloaddition. The presence of a small peak at 288 eV is typically assigned to C=O species, but may be attributed to adsorbed organic solvent from the post-reaction washes. Successful attached of the dopant molecule through the formation of a [1,2,3]-triazole ring is confirmed by the N *1s* core-level scan shown in **Figure 3(b)**.^{40,41} A large, broad peak primarily centred at 401 eV in the N *1s* core level spectrum is indicative of the presence of distinct nitrogen environments which strongly support the bonding of the azido group to the terminal alkyne. The small satellite peak centered near 405 eV, may be associated with adsorbed DPPA species.⁴² Due to the overlap of the Si *2p* plasmon with the P *2p* photoelectric line, it is non-trivial to determine the presence of P on the surface using XPS alone but the presence of the DPPA molecule on the surface can be determined indirectly using the C *1s* and N *1s* core level spectra. XPS spectra showed no evidence of Cu *2p* peaks, typically observed at a binding energy of 932 and 952 eV respectively, highlighting complete removal of the copper catalyst post-reaction and prior to the rapid-thermal-anneal treatments.⁴³

Click modification of the 1,7 octadiyne functionalized Si surface with arsenic azide (AA)

A strategy analogous to that used in the functionalisation of Si (100) with the DPPA molecule was performed using the synthesized arsenic azide (AA). **Figure 4(a)** shows a Si *2p* core level scan of a Si substrate functionalized with 1,7-octadiyne, followed by attachment of the AA

molecule *via* an alkyne-azide cycloaddition. A small level of oxide (< 1 at.%) was observed which may be associated with traces of water from the sodium azide activation procedure.⁴⁴ The low amount of oxide detected did not significantly impact on the incorporation of surface dopant.⁴⁵ **Figure S2(b)** shows an XPS survey spectrum indicating the presence of Si, C, O and As which is indicative of an AA functionalized surface. **Figure 4(b)** displays a C *1s* core level spectrum of the AA functionalized surface. Similar to the DPPA functionalized substrate, the spectrum consists of a broad peak centered at 285 eV which indicates the presence of C-C bonds. A smaller feature centered at ~287 eV shows the presence of a C-N structure consistent with the establishment of a [1,2,3]-triazole aromatic ring.⁴⁶ The binding energy is in good agreement with previous C-N binding energy values reported by Böcking *et al.* **Figure 4(c)** shows the N *1s* core level spectrum deconvoluted into two peaks. A broad peak centered at ~401 eV can be assigned to the different chemical environments of the N atoms in the triazole ring, which was fitted using similar parameters to the DPPA functionalized surface shown in **Figure 3(b)** to confirm successful coupling of the azide to the terminal alkyne. The second feature at ~ 405 eV is chemically shifted by ~ 4 eV with respect to the primary peak, which is indicative of inorganic N species. This may be attributed to the electron-deficient nitrogen of the azide group.^{42,47} **Figure 4(d)** shows the As *2p* core level scan after functionalization with the AA molecule. The peak at approximately 1328 eV is shifted to a higher binding energy with respect to the elemental arsenic binding energy of ~1323 eV.⁴⁸ Since photoelectric lines related to Cl were not detected, the presence of AsCl₃ on the surface was excluded. Assuming the alkyne-azide cycloaddition occurs at one out of the three azide groups on the AA molecule, this shift in the binding energy may be attributed to the highly electron-deficient nature of the two remaining azide groups bonded to the arsenic of the AA molecule.

Stability of the functionalized InGaAs samples toward ambient conditions

The stability that is inferred on Si surfaces by grafted monolayers is interesting for many applications. With respect to device integration, regrowth of Si oxides prior to rapid-thermal-anneal treatment and other important steps in CMOS processing is not desirable, especially in the moments immediately after a processing step. Surface functionalization greatly increases the oxidation resistance of Si.²⁵ To ascertain the stability of the “click” functionalized samples towards ambient conditions, substrates were left exposed to ambient conditions (air, 20 °C) for periods of time ranging from 24 h to one month. Prior to analysis the samples were rinsed with chloroform to remove adventitiously adsorbed material from the surface. The Si 2*p* core level scan was used to monitor for an increase in oxide formation. **Figure 5** shows an overlay of data acquired after 24 h on a non-functionalized sample, an AA-functionalised sample and a DPPA functionalized sample. Both of the functionalized samples showed no presence of oxide after 24 h. The non-functionalized sample shows a slight presence after being left out in ambient conditions for 24 h. The complete acquired stability spectra for the DPPA functionalized samples are shown in **Figure S3(a-d)** (see Supporting Information). Comparative spectra for the blank, non-functionalized Si substrates are shown in **Figure S4(a-d)** (See Supporting Information). The DPPA-functionalized substrates exhibited excellent resistance towards re-oxidation when compared to the non-functionalized Si substrates, especially 24 h immediately after functionalization. This stability can be attributed to the tight packing of the initially grafted alkyne layer. **Figure S5(a-d)** (see Supporting Information), compares the Si 2*p* XPS spectra for AA functionalized samples, acquired immediately after preparation and after exposure to ambient conditions ranging from 24 h, 1 week and 1 month. These samples also displayed strong resistance towards re-oxidation in comparison to the non-functionalized Si substrate. In

addition to the influence of the tightly packed alkyl chain on these substrates, the increased oxidation resistance could be attributed not only to the smaller molecular footprint of the AA molecule allowing improved packing post-functionalisation, but also to the use of the alkyne primary passivation layer. These short chain linear molecules have excellent stability and packing characteristics. In addition, especially in the case of DPPA, the pi-pi interactions between the two aromatic rings on adjacent DPPA molecules on the surface greatly improve molecular packing to ensure the underlying Si substrate is protected.⁴⁹

Dopant profiling

Samples were capped with a 50 nm layer of SiO₂ *via* sputtering and transferred to a rapid-thermal-anneal tool where the substrates were subjected to a 5 s anneal at 1050 °C, based on parameters from our previous work and other P-MLD reports⁵⁰, under a nitrogen atmosphere. The cap was removed using a buffered-oxide-etch at 20 °C and samples were cleaned by sonication in chloroform and toluene prior to electrochemical capacitance-voltage (ECV) analysis. The specific composition of the capping layer and the method used for depositing the capping layer can change the monolayer integrity and may influence the diffusion process, but the effect of the capping layer was not studied in this work. To compare the “click” functionalization strategy used in this work to a traditional phosphorus MLD approach, which typically uses a hydrosilylation reaction between the Si-H surface and an organic carbon-based dopant-containing molecule, a Si sample was functionalized with a non-azide precursor, allyldiphenyl phosphine (ADP) *via* a thermally-induced hydrosilylation reaction (details in Supporting Information). This molecule was chosen as it is structurally similar to the diphenylphosphoryl azide molecule employed in the CuAAC click reaction but does not contain

an azide functional group; instead undergoing a hydrosilylation reaction between the H-terminate Si surface and C=C labile site on the ADP molecule. The RTA parameters were kept identical for the two samples.

Figure 6(a) displays an ECV profile of a DPPA functionalized Si substrate which has been thermally treated using RTA. As can be seen from the profile, the peak active carrier concentration was approximately 1×10^{19} atoms/cm³ with the highest concentration at depths less than 25 nm. **Figure 6(b)** shows the ECV profile for a Si substrate which has been functionalized with ADP and subjected to the same RTA recipe as the DPPA-functionalized sample. The ECV profiles for surface prepared by the click chemistry method and the MLD method are quite similar with both exhibiting a peak active carrier concentration of 1×10^{19} atoms/cm³. This similarity between carrier concentrations may be attributed to the packing characteristics of the DPPA and ADP molecules. Additionally, as shown in **Figure S6** (see Supporting Information), the ADP-functionalized surface oxidized more quickly in ambient conditions, especially within the first 24 h, when compared to the Si samples which had initially been functionalized with the dialkynes. As they are structurally similar, packing densities and conformations would be expected to be quite close, leading to monolayers with identical steric features. Samples were prepared using dialkynes varying in length between six carbons and ten carbons with each chain being functionalized subsequently with the DPPA molecule using identical conditions each time. No difference in carrier concentration was observed for samples with the shortest carbon chain lengths and the longest carbon chain lengths. This shows that using a primary passivation layer in conjunction with the dopant-containing molecule allows much improved oxidation resistance without affecting the diffusion of the dopant atoms.

Similar rapid thermal anneal treatments were applied to the Si substrates which were functionalized using the arsenic azide molecule. Characterization of these surfaces *via* ECV analysis was challenging as the resultant light doping was not amenable to efficient etching for the depth profiling. **Figure 7** shows the ECV profile of an AA-functionalized Si substrate thermally treated using RTA for 5 s at 1050 °C. Peak carrier concentrations approached 2×10^{18} atoms/cm³ at depths of less than 25 nm. We have recently reported MLD on Si using a traditional carbon-based As-containing precursor in conjunction with a thermally-initiated hydrosilylation reaction and achieved excellent in-diffusion coupled with high chemical concentrations approaching 2×10^{20} atoms/cm³.⁴⁵ The lower carrier concentration for arsenic observed in this work is unlikely due to diffusion suppression. Nitrogen has been reported to suppress diffusion of As in Ge⁵¹ and also suppression of B in Si⁵² but has not been reported to suppress the diffusion of As in Si. The lower observed carrier concentration is more likely to be attributed to poor yields of the alkyne-azide fusion reaction. The effect of steric constraints is well known from solution-based chemistry especially for larger molecular systems.⁵³ In this study, the effect is more pronounced due to one end of the alkyne being anchored to the surface of the Si⁵⁴, which requires the arsenic azide molecule to approach the terminal alkyne at a certain orientation. To obtain higher carrier concentrations requires the close packing of the azides on the surfaces. Despite the small molecular footprint of the arsenic azide molecule, the highly charged and linear structures of azide groups attached to the arsenic may introduce steric effects at the interface that do not allow for close packing. This effect is somewhat negated on the DPPA molecule due to the presence of only one azide group, with the packing densities dominated by the large heteroaryl moieties present. The “click” reaction yield between the

arsenic azide and acetylene-terminated Si surface was estimated by comparing the C-N/C-C elemental ratios as obtained from XPS measurements. In order to simplify the curve-fitting needed to make the estimate, the C-O and C-N components were represented by one peak at approximately 286.5 eV, with the ratio reflecting the amount of arsenic azide attached to the acetylene-terminated surface, using a method described by Li *et al.*⁵⁵ An elevated temperature of 70 °C was used in an attempt to increase the yield. Using this method, a 59 % conversion yield was estimated for the reaction between arsenic azide and the acetylene-terminated Si surface. This may be attributed to the sterically-hindered nature of the rigid and charged azide groups on the arsenic azide molecule. Light As doping may be of use for applications in devices where low defect densities are required to minimise dark currents such as high operating temperature detectors and low-capacitance photodiodes for electron detection^{56,57} Similarly to the DPPA-doped substrates, there was no discernible difference in carrier concentrations for samples with the shortest carbon chain lengths and the longest carbon chain lengths.

Conclusions

Controlled doping at the nanoscale has become progressively more difficult in recent years as device feature sizes have reduced. There is a need for innovative and reliable methods for the doping of Si while preventing significant re-oxidation of the underlying substrate. Si was successfully functionalized with di-alkynes with chain lengths between 6 and 10 carbon atoms and then subsequently functionalized *via* a copper-catalyzed azide-alkyne cycloaddition reaction to give a dopant-containing monolayer on the surface. XPS spectra contained signals referring to the [1,2,3]-triazole ring formation indicating successful incorporation of the dopant-containing azides to the terminal acetylene groups. ECV measurements confirmed successful diffusion of

the dopants into the Si substrate with the P-doping process being most effective. The substrates also exhibited excellent resistance toward re-oxidation especially in the immediate 24 h post-functionalisation. The experimental procedure is robust, particularly the dopant molecule introduction *via* the Huisgen 1,3-dipolar cycloaddition. The procedure is insensitive to reaction conditions that would halt traditional MLD reactions such as the presence of trace water and oxygen. The presence of either could potentially oxidize the Si surface and affect the attachment of the dopant-containing monolayer and allows for the introduction of dopant-containing moieties using milder reaction conditions than previously reported. This work also utilized the beneficial application of tightly-packed terminal acetylene monolayers which provide the aforementioned increased resistance to oxidation.

Acknowledgement

The Authors acknowledge financial support from Science Foundation Ireland (Grant: 09/IN.1/I2602).

Supporting Information Available: Reaction schematics, ADP functionalisation procedure and schematics, additional XPS spectra and XPS stability spectra are available in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org/>

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Figures

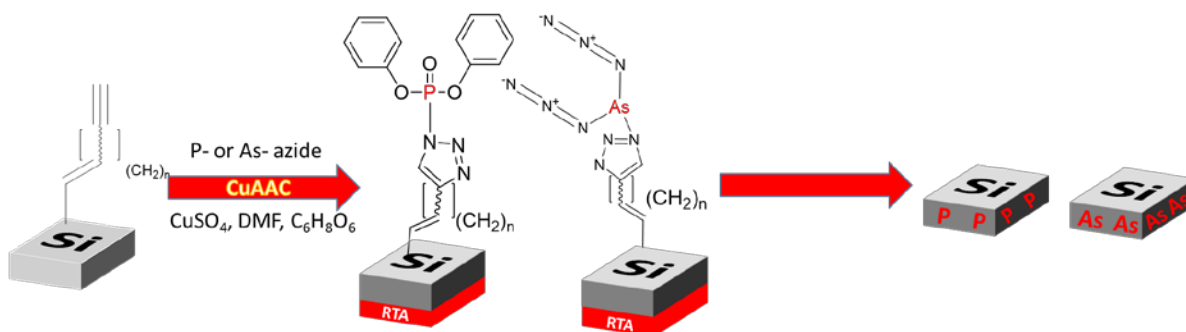


Figure 1. Schematic showing the functionalization and doping strategy employed in this study.

A silicon sample previously functionalized with a dialkyne *via* thermal hydrosilylation is immersed in a solution of a dopant-containing azide, copper sulfate, DMF and ascorbic acid where an alkyne-azide cycloaddition occurs to form a dopant containing monolayer on the Si surface. These samples are then capped with SiO_2 , and subjected to a rapid thermal anneal of 1050°C for 5 s and the cap is subsequently removed to give shallow doped Si.

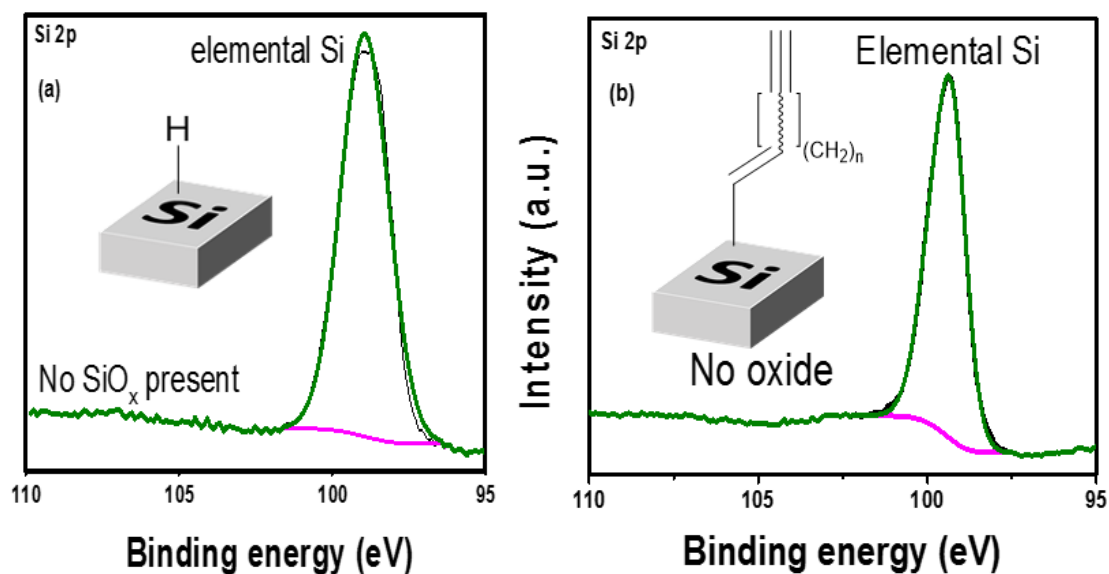


Figure 2. (a) Si 2p core level scan from a Si substrate after a standard RCA clean and HF etch with a primary peak at ~99 eV highlighting complete removal of the surface oxides. (b) Si 2p core level scan of a Si substrate functionalized with 1,7 octadiyne. No evidence of any Si oxides are present post-functionalisation, indicating a pristine surface ready for subsequent derivatization of the terminal alkyne with the DPPA molecule.

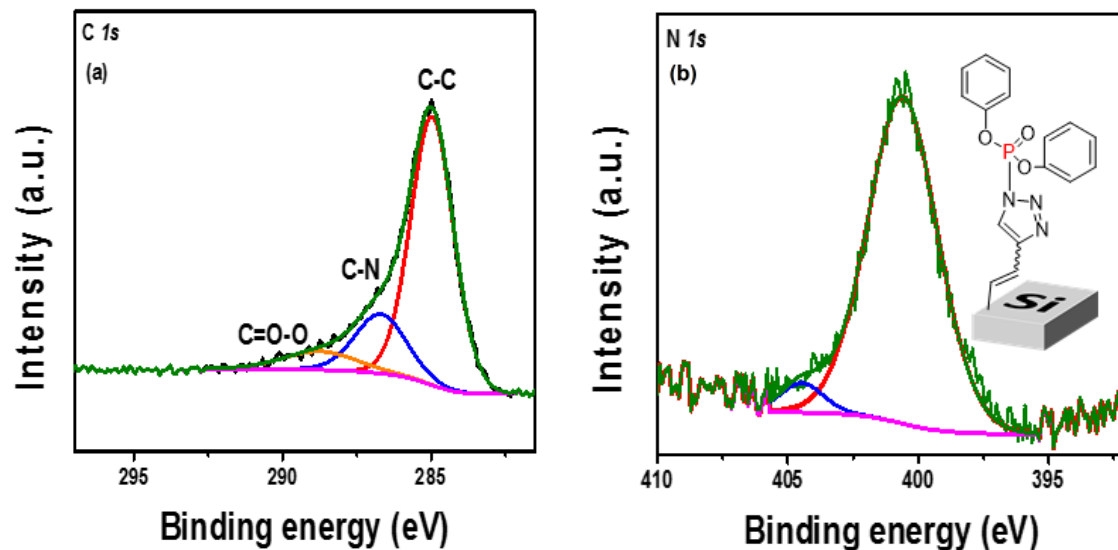


Figure 3. (a) Deconvoluted C *1s* core level spectrum for the DPPA functionalized Si sample. The peaks corresponding to the C-N and C-C groups in the moiety are labelled and shown in blue and red respectively. (b) Deconvoluted N *1s* core level scan with peaks confirming the presence of the [1,2,3]-triazole ring, shown in red, which is characteristic of the alkyne-azide cycloaddition with the diagram representing the surface functionalized with the DPPA molecule. The component in blue represents adsorbed DPPA molecule

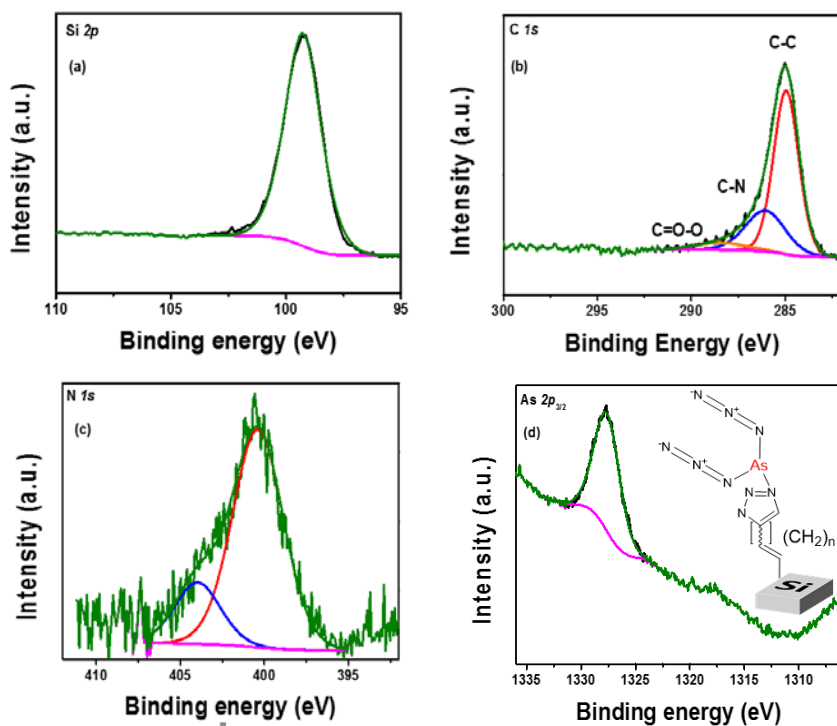


Figure 4. (a) Si 2*p* core-level spectrum of a 1,7-octadiyne functionalized Si wafer prior to subsequent functionalisation with the arsenic azide (AA) molecule. (b) Deconvoluted C 1*s* core level spectrum of a Si sample functionalized with 1,7-octadiyne and subsequently derivatised with the arsenic azide molecule with components corresponding to C-C and C-N moieties labelled. (c) N 1*s* core level spectrum showing a primary peak centred at ~401 eV indicative of the triazole ring formation and satellite peak at ~405 eV signifying the presence of azide groups. (d) As 2*p*_{3/2} core level XPS scan showing the presence of As on the surface post-reaction.

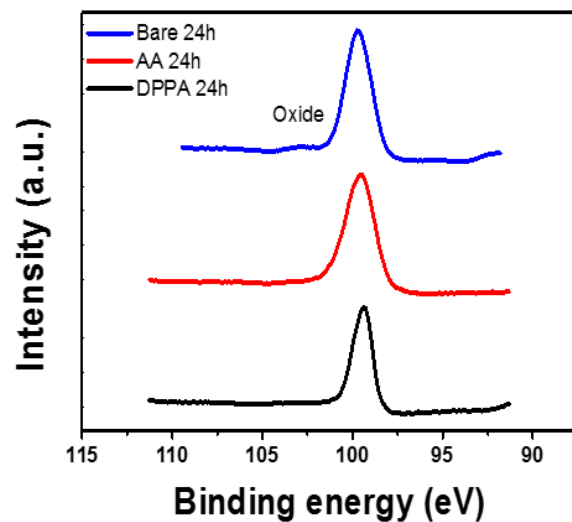


Figure 5. Si 2p core level scans showing stability data acquired on samples left out in ambient conditions for 24 h. The DPPA-functionalised samples shown in black and the AA-functionalised sample shown in red show no presence of oxide. The non-functionalised sample shown in blue exhibits a slight presence of oxide after 24 h in ambient conditions, located at approximately 103 eV.

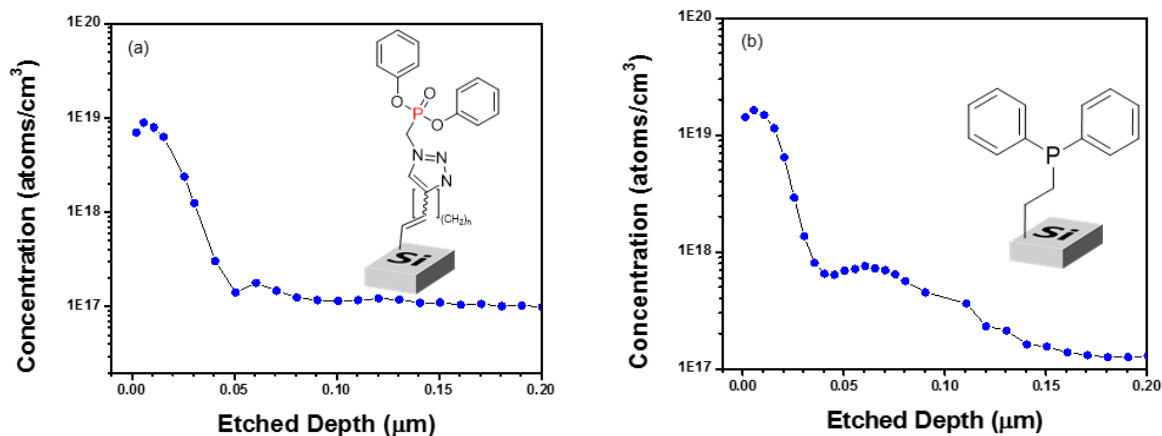


Figure 6. ECV profiles for (a) a sample functionalized with DPPA and subsequently thermally annealed at 1050 °C for 5 s and (b) a sample functionalized with ADP and then subsequently subjected to rapid-thermal-anneal treatment at 1050 °C for 5 s. Both samples exhibited similar dopant profiles with peak concentrations at approximately 1×10^{19} atoms/cm³ measured with highest concentrations occurring at shallow depths less than 25 nm. Inset depicts the surface chemistry.

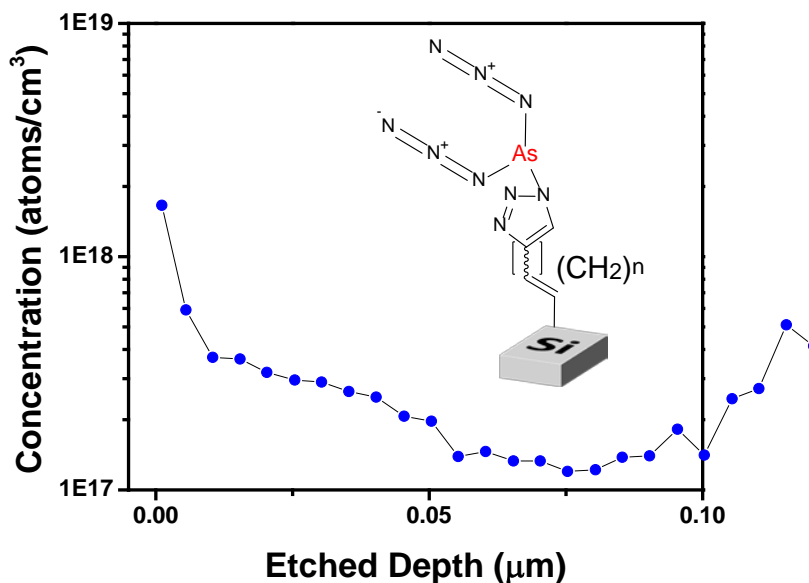


Figure 7. ECV profile for a sample functionalized with 1,7-octadiyne and subsequently functionalized with the AA molecule. The substrate was capped and subjected to rapid-thermal-anneal treatment at 1050 °C for 5 s. The sample exhibited a peak concentration approaching 2×10^{18} atoms/cm³ with peak concentrations occurring at shallow depths less than 20 nm. Inset represents the AA-functionalized surface.

TOC Graphic

