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First Principles Simulation of Amorphous Silicon
Bulk, Interfaces, and Nanowires for Photovoltaics

By

Merid Legesse Belayneh

Supervisors: Dr. Michael Nolan and Dr. Georgios Fagas
Head of Department: Prof. Martyn Pemble

A thesis submitted to the
NATIONAL UNIVERSITY OF IRELAND, CORK
College of Science, Engineering & Food Science Department of Chemistry
Tyndall National Institute for the degree of

Doctor of Philosophy

January 2015
This thesis is dedicated to the memory of my beloved sister, Tsigereda Legesse (Muna). She is passed way before finished her education. I am truly saddened by her passing and her memories will always remain with me.
Acknowledgement

First and foremost, I would like to express my sincere gratitude to my supervisors: Dr. Michael Nolan and Dr. Giorgos Fagas for the continuous support of my Ph.D. study and research, for their patience, motivation, enthusiasm, and immense knowledge. Their guidance helped me in all the time of research and writing of this thesis. I could not have imagined having better supervisors and mentors for my Ph.D. study.

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I would like to thanks to the European Commission, through the 7th Framework ICT-FET-Proactive program, Project: SiNAPS (contract no 257856) and the Science Foundation Ireland (SFI) Research Grant Program, project “EMOIN” grant number SFI 09/SIRG/I1620 for financial support. I also acknowledge computing resources provided by SFI to the Tyndall National Institute and by the SFI and Higher Education Authority Funded Irish Centre for High End Computing.

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# LIST OF ACRONYMS

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<tr>
<th>Acronym</th>
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<tr>
<td>AFORS</td>
<td>Automat for simulation of heterostructures</td>
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<tr>
<td>a-Si</td>
<td>Amorphous silicon</td>
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<tr>
<td>a-Si:H</td>
<td>Hydrogenated amorphous silicon</td>
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<tr>
<td>c-Si</td>
<td>Crystalline silicon</td>
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<td>CFSYS</td>
<td>Constant final state yield spectroscopy</td>
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<tr>
<td>CRN</td>
<td>Continuous random network</td>
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<tr>
<td>C-V</td>
<td>Capacitance voltage</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<td>DOS</td>
<td>Density of states</td>
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<td>FET</td>
<td>Field effect transistor</td>
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<td>GeNW</td>
<td>Germanium nanowire</td>
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<td>GGA</td>
<td>General gradient approximation</td>
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<td>GULP</td>
<td>General utility lattice program</td>
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<td>HF</td>
<td>Hartree-Fock</td>
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<td>HIT</td>
<td>Heterojunction with Intrinsic Thin layer</td>
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<td>IPE</td>
<td>Internal photoemission spectroscopy</td>
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<td>IPHT</td>
<td>Institute of Photonic Technology</td>
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<td>IPR</td>
<td>Inverse participation ratio</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<td>I-V</td>
<td>Current voltage</td>
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<td>KS</td>
<td>Kohn-Sham</td>
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<td>LCD</td>
<td>Liquid crystal display</td>
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<td>LDA</td>
<td>Local density approximation</td>
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<td>MD</td>
<td>Molecular dynamics</td>
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<td>NVE</td>
<td>Constant energy and constant volume</td>
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<td>PAW</td>
<td>Projector augmented-wave</td>
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<td>PDOS</td>
<td>Projected density of states</td>
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<td>Acronym</td>
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<tr>
<td>PVCVD</td>
<td>Plasma-enhanced chemical vapor deposition</td>
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<td>PPs</td>
<td>Pseudopotentials</td>
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<td>PV</td>
<td>Photovoltaics</td>
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<td>QR</td>
<td>Quench rate</td>
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<td>RDF</td>
<td>Radial distribution function</td>
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<td>RF</td>
<td>Radio Frequency</td>
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<tr>
<td>SCF</td>
<td>Self-consistent field</td>
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<td>SFI</td>
<td>Science Foundation Ireland</td>
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<tr>
<td>SiNW</td>
<td>Silicon Nanowire</td>
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<td>SR</td>
<td>Spectral response</td>
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<td>SWE</td>
<td>Staebler–Wronski effect</td>
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<td>TA</td>
<td>Transverse acoustic</td>
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<td>TO</td>
<td>Transverse optical</td>
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<tr>
<td>VDOS</td>
<td>Vibrational density of states</td>
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<tr>
<td>VASP</td>
<td>Vienna ab-initio simulation package</td>
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<tr>
<td>VBM</td>
<td>Valence band maxima</td>
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I, Merid Legesse Belayneh, certify that this thesis is my own work and I have not obtained a degree in this university or elsewhere on the basis of the work submitted in this thesis.

Merid Legesse Belayneh
Abstract

Amorphous silicon has become the material of choice for many technologies, with major applications in large area electronics: displays, image sensing and thin film photovoltaic cells. This technology development has occurred because amorphous silicon is a thin film semiconductor that can be deposited on large, low cost substrates using low temperature. In this thesis, classical molecular dynamics and first principles DFT calculations have been performed to generate structural models of amorphous and hydrogenated amorphous silicon and interfaces of amorphous and crystalline silicon, with the ultimate aim of understanding the photovoltaic properties of core-shell crystalline amorphous Si nanowire structures. We have shown, unexpectedly, from the simulations, that our understanding of hydrogenated bulk a-Si needs to be revisited, with our robust finding that when fully saturated with hydrogen, bulk a-Si exhibits a constant optical energy gap, irrespective of the hydrogen concentration in the sample. Unsaturated a-Si:H, with a lower than optimum hydrogen content, shows a smaller optical gap, that increases with hydrogen content until saturation is reached. The mobility gaps obtained from an analysis of the electronic states show similar behavior. We also obtained that the optical and mobility gaps show a volcano curve as the H content is varied from 7% (undersaturation) to 18% (mild oversaturation). In the case of mild over saturation, the mid-gap states arise exclusively from an increase in the density of strained Si-Si bonds. Analysis of our structures shows the extra H atoms in this case form a bridge between neighboring silicon atoms which increases the corresponding Si-Si distance and promotes bond length disorder in the sample. That has the potential to enhance the Staebler-Wronski effect.

Planar interface models of amorphous-crystalline silicon have been generated in Si (100), (110) and (111) surfaces. The interface models are characterized by structure, RDF,
electronic density of states and optical absorption spectrum. We find that the least stable (100) surface will result in the formation of the thickest amorphous silicon layer, while the most stable (110) surface forms the smallest amorphous region. We calculated for the first time band offsets of a-Si:H/c-Si heterojunctions from first principles and examined the influence of different surface orientations and amorphous layer thickness on the offsets and implications for device performance. The band offsets depend on the amorphous layer thickness and increase with thickness. By controlling the amorphous layer thickness we can potentially optimise the solar cell parameters.

Finally, we have successfully generated different amorphous layer thickness of the a-Si/c-Si and a-Si:H/c-Si 5 nm nanowires from heat and quench. We perform structural analysis of the a-Si-/c-Si nanowires. The RDF, Si-Si bond length distributions, and the coordination number distributions of amorphous regions of the nanowires reproduce similar behaviour compared to bulk amorphous silicon.

In the final part of this thesis we examine different surface terminating chemical groups, -H, -OH and –NH$_2$ in (001) GeNW. Our work shows that the diameter of Ge nanowires and the nature of surface terminating groups both play a significant role in both the magnitude and the nature of the nanowire band gaps, allowing tuning of the band gap by up to 1.1 eV. We also show for the first time how the nanowire diameter and surface termination shifts the absorption edge in the Ge nanowires to longer wavelengths. Thus, the combination of nanowire diameter and surface chemistry can be effectively utilised to tune the band gaps and thus light absorption properties of small diameter Ge nanowires.
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CHAPTER 1

1 Introduction and summary

1.1 Introduction

One of the biggest issues facing our planet is the energy problem. Recent price increases in oil and natural gas as well as geographical issues impacting on oil producing nations and climate change have highlighted a pressing need for alternative energy sources. Among the alternatives to fossil fuels is to use solar energy and energy sources like geothermal energy, wind and hydrogen energy. These energy sources not only provide energy; they are also more environmentally friendly and cleaner than fossil fuels, with fewer repercussions for the planet. Solar cells are one of the most promising candidates to reduce the energy problem as well as the environmental issues. According to international energy agency (IEA) report since 2010, the world has added more solar photovoltaic (PV) capacity than in the previous four decades. Total global PV capacity overtook 150 gigawatts (GW) in early 2014. The two IEA technology roadmaps also show how solar photovoltaic (PV) systems could generate up to 16% of the world’s electricity by 2050 while solar thermal electricity (STE) from concentrating solar power (CSP) plants could provide an additional 11%. Combined, these solar technologies could prevent the emission of more than 6 billion tonnes of carbon dioxide per year by 2050.

Focusing on solar, solar cells are devices that convert solar energy to electrical energy. The process in which the solar cell converts solar energy to electricity is called photovoltaics (PV). A Schematic picture is shown in figure 1.1. Photovoltaic devices generate electricity directly from sunlight via an electronic process that occurs naturally in certain types of
materials, called semiconductors. Electrons in these materials are freed by solar energy and can be induced to travel through an electrical circuit, powering electrical devices or sending electricity to the grid. Traditional solar cells are mostly made out of silicon, a well-known semiconductor. When light energy strikes the solar cell, electrons are knocked loose from the atoms in the semiconductor material. If electrical conductors are attached to the positive and negative sides, forming an electrical circuit, the electrons can be captured in the form of an electric current - that is, electricity. This electricity can then be used to power a load, such as a light or a tool.

While it is the leading solar cell material, Si is brittle and fractures at very small deformation. This poses a significant challenge to make and handle large area solar cell panels and associated costs. To further reduce the cost to harvest solar energy, there have been emerging efforts on developing thin film solar cells that can be fabricated on thin plastic foils by a roll-to-roll process. The functional device material used in such thin film solar cells include amorphous silicon, organics/polymer film, gallium arsenide, copper-indium selenide, etc.

Figure 1.1 Schematic of a photovoltaic cell.
Among the materials which have been used for the last four decades in making thin film solar cells are amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H). a-Si is a material of tremendous interest from both a fundamental perspective, as the prototype of disordered materials, and from a technology perspective, as the key material in the ubiquitous thin film displays in modern ICT devices, as well as in next generation solar cells. In fact, there is renewed and increasing interest in the optical absorption properties of hydrogenated a-Si owing to its use in high-efficiency up to 23 % heterojunction solar cells\textsuperscript{2,3,4,5,6,7,8,9,10,11,12}.

a-Si is a randomly ordered form of silicon where there is no periodicity in the arrangement\textsuperscript{1} of the silicon atoms. A schematic picture of a-Si is shown in figure 1.2. The lack of atomic order means that not all silicon atoms form bonds with four silicon neighbours as in bulk crystalline Si. Therefore some bonding sites on the silicon are free, which are referred to as dangling bonds. These bonds can be passivated with hydrogen atoms to form hydrogenated amorphous silicon (a-Si:H), which is used for solar cell fabrication. The high absorption coefficient of photons in its absorption range (1.6 to 1.9 eV) means that together with lower cost and large area production a thin film layer of amorphous silicon can be used for solar cell applications\textsuperscript{13,14,15}.

1.2 Schematic picture of the atomic structure in amorphous silicon.
Experimentally, there exist several preparation methods for a-Si:H films. A well known method for the deposition of amorphous silicon is plasma-enhanced chemical vapor deposition (PECVD). In experiment the deposition process takes place in the reaction chamber. Due to this a detailed understanding of the role of hydrogen incorporation into the silicon host remains a challenge. The amount of hydrogen needed to passivate the dangling silicon, its influence on the electronic and optical properties and on the amorphous network, and the relation to the Staebler-Wronski effect\textsuperscript{16}, the well known efficiency degradation during exposure to sunlight, are open fundamental questions that link the chemical composition and structure to continuous improvements in device performance. In particular, studies of the optical properties, which determine the energy absorption in a solar cell, and their dependence on hydrogen content and disorder in a-Si:H have led to some conflicting interpretations in the literature regarding the effect of hydrogenation on the optical band gap, understanding the effect of surface orientations and amorphous layer thickness on electronic, optical and band offsets are still a challenge in thin film devices. In this thesis, I used empirical potentials and first principles simulations with density functional theory (DFT) to investigate the properties of amorphous silicon (a-Si), a-Si:H, the interface between a-Si:H/c-Si and a-Si/c-Si core-shell nanowires. The nanowires used in solar cells fabricated experimentally\textsuperscript{17,18,19,20,21,22} are composed of a crystalline Si core surrounded by an amorphous Si shell; another interesting material that I have studied is crystalline Germanium nanowires (GeNWs) with different surface termination to modify the optical gap of the NWs. The models studied in the thesis range from pure bulk a-Si to a-Si/c-Si core-shell nanowires allowing an examination of the fundamental properties of those materials.
In this thesis, a-Si is generated by melting crystalline Si (c-Si) and quickly quenching to trap the amorphous structure, which is then characterised with, e.g. the radial distribution function, bond angle and length distribution, phonon dispersion. The electronic and optical properties are explored as a function the a-Si quenching rate; there is some evidence that the timescales of the quenching can impact on the electronic structure of a-Si\textsuperscript{23}, I also examine this possibility in chapter 3. I generate a-Si:H by incorporating hydrogen in a quenched a-Si structure and relax using DFT.

In general, in this thesis I studied the electronic and optical properties of hydrogenated amorphous silicon (a-Si), the effect of surface orientation and amorphous layer thickness on band offset, electronic and optical properties of the interface between amorphous and crystalline silicon, structural analysis of a-Si core/c-Si shell nanowires and finally modifying the band gap and optical properties of Germanium nanowires by surface termination.

### 1.2 Summary and Outline of the work

The aim of the thesis is to undertake first principles simulations of the optical and electronic properties of bulk a-Si:H and a-Si:H/c-Si structures using atomic structural models to allow for a rational understanding a-Si:H solar cell performance.

I have shown, unexpectedly, that our understanding of hydrogenated bulk a-Si needs to be revisited, with our robust finding that when fully saturated with hydrogen, bulk a-Si exhibits a constant optical energy gap, irrespective of the hydrogen concentration in the sample. The previous consensus has been that the optical gaps increase with H content. Unsaturated a-Si: H, with a lower than optimum hydrogen content, shows a smaller optical gap, that increases with hydrogen content until saturation is reached. The mobility gaps obtained from an analysis of the electronic states show similar behaviour.
The optical and mobility gaps show a volcano curve as the hydrogen content varies from undersaturation to mild oversaturation, with largest gaps obtained at the saturation hydrogen concentration. At the same time, mid-gap states associated with dangling bonds and strained Si-Si bonds, which are longer than the equilibrium Si-Si distance, disappear at saturation but reappear at mild oversaturation which is consistent with the evolution of optical gap. The distribution of Si-Si bond distances and the strained Si-Si bonds provide the key to the change in electronic properties. In the undersaturation regime the new electronic states in the gap arise from the presence of dangling bonds and strained Si-Si bonds. Increasing hydrogen concentration up to saturation reduces the strained bonds and removes dangling bonds. In the case of mild oversaturation the mid-gap states arise exclusively from an increase in the density of strained Si-Si bonds. The extra hydrogen atoms form a bridge between neighbouring silicon atoms, thus increasing the Si-Si distance and increasing disorder in the sample. That has the potential to enhance the Staebler-Wronski effect.

Planar interface models of amorphous-crystalline silicon have been generated in Si (100), (110) and (111) surfaces. The interface models are characterised by structure, radial distribution function, electronic density of states and optical absorption spectrum. We find that the least stable (100) surface will result in the formation of the thickest amorphous silicon layer, while the most stable (110) surface forms the smallest amorphous region. Analysis of the RDF indicates a structural interface region one layer thick in both a-Si/c-Si and a-Si:H/c-Si interface, while the electronic density of states shows new states forming as a result of disorder, even in the seemingly crystalline layers (as identified by RDF), indicating that an electronic interface is formed between a-Si (and a-Si:H) and c-Si that is larger than the structural interface. Finally computed optical absorption spectra demonstrate that for thick amorphous layers, the optical absorption is dominated by a-Si, while thinner layers show an
optical absorption spectrum characteristic of crystalline silicon, but modified by the presence of the a-Si layer and this is driven by the stability of the crystalline Si surfaces. The (100) a-Si:H/c-Si interface model has a computed DFT optical band gap around 1.25 eV, independent of the precise thickness of the amorphous region. Overall, the stability of the surface determines the detailed properties of the structural and electronic interfaces. We have also looked at band offsets of a-Si:H/c-Si heterojunctions and discuss the influence of different surface orientations and amorphous layer thickness on the offsets and implications for device performance. In general, when the thickness of the a-Si:H layer increases the valence band offsets also increase, to a converged value of 0.65 eV consistent with experiment. The size of the increment is different in the case of valence and conduction band offsets with thickness of the a-Si:H layers. This is because the a-Si:H thickness affects the valance band edge more than the conduction band edge. To investigate the effect of surface orientation on band offset, we have prepared the same amorphous/crystalline proportions (48%-a-Si:H-52%-c-Si) in the (100) and (111) surface of a-Si:H/c-Si interfaces. Valence band offsets are calculated to be 0.58 and 0.59 eV and the conduction band offsets are 0.12 eV and 0.16 eV for (100) and (111) respectively. This result clearly shows that the orientation of the surface has no significant impact on changing the band offset of a-Si:H/c-Si interfaces. From this we conclude that whatever orientations we use for solar cell fabrication, the band offsets cannot be significantly affected. However, the thickness of the amorphous layer plays an important role to engineer the band offsets. We know that from our results, band offsets depend on the amorphous layer thickness. By controlling the amorphous layer thickness we can potentially optimize the solar cell parameters.

From our final activity we have successfully generated different amorphous layer thickness a-Si/c-Si core-shell nanowires. The Si nanowire model is oriented along the (100) direction, has
a diameter of 5 nm (which is the limit of the available computing resources but large enough to be stable in the heat and quench process), periodic along the length of the wire (z-axis), with a three unit cell repeat unit and enough vacuum in the x- and y-directions to isolate the nanowire. This nanowire model has a hexagonal cross-section and exposes (111) and (100) surfaces, which based on our investigation in surface stability in interface models, suggests that during melting simulations, thicker disordered regions could form at the (100) facets than at the (111) facets, similar to the planar interfaces. The a-Si/c-Si core-shell structures are then characterized by structural properties (radial distribution functions, coordination number distribution, Si-Si distance distribution) for all model structures. For the electronic and optical properties we only focus for the thinnest amorphous layer thickness of the core-shell structure. One reason for this is that our model structures have large 5 nm diameter and it takes significant computational time to optimize the 960 atom structures with H and vacuum using DFT. We have also considered small diameter (down to 1nm nanowires) but they are not of sufficient size to represent the core-shell nanowires, and we also find that the nanowires are very sensitive to the diameter in the melting process. This means that for 2600 K melting temperature the atoms in the system are completely disordered after a quench never relax to any kind of useful structure. Due to the above reasons, we have only presented initial results of core-shell nanowires which nonetheless are a very useful next step in research activities on the core-shell NWs.

Germanium nanowires have received particular attention because of the important role played by this materials system in contemporary microelectronics and the potential for applications ranging from novel electronic devices to molecular level sensing and to solar energy harvesting. Our work shows that the diameter of Ge nanowires and the nature of surface terminating groups both play a significant role in the magnitude and the nature of the
nanowire band gaps, allowing tuning of the band gap by up to 1.1 eV. We also show for the first time how the nanowire diameter and surface termination shifts the absorption edge in the Ge nanowires to longer wavelengths. Thus, the combination of nanowire diameter and surface chemistry can be effectively utilized to tune the band gaps and thus light absorption properties of small diameter Ge nanowires.

The results in this thesis provide an important milestone to further analyze the properties of a-Si:H/c-Si heterostructures prepared with different thicknesses of amorphous silicon and various conditions of sample preparation, which is important for understanding and optimizing the light absorption and charge dynamics of a-Si:H/c-Si solar cell heterostructures.

In particular, we have presented new and fundamental insights into (I) the role of hydrogen on the optical and electronic properties of a-Si:H, (II) the electronic and optical properties of the a-Si:H/c-Si heterojunction and band alignment between amorphous and crystalline silicon interface, (III) structural characterization of crystalline silicon core-amorphous silicon shell silicon nanowires, and (IV) modifying the band gap of germanium nanowires by surface termination.

The structure of the thesis is as follows. In Chapter 2 we present a literature review on hydrogenated amorphous silicon and a-Si:H/c-Si. In this chapter we looked at the details of literature review for a better understanding of current state of the art in a-Si:H interface between a-Si/c-Si, a-Si/c-Si core-shell nanowires and Ge nanowires. In chapter 3, the theoretical background is discussed. The preparation of our models is discussed in detail using classical molecular dynamics (MD) and density functional theory (DFT) (with both general gradient approximation (GGA) and hybrid DFT). We use a standard heat and quench approach to generate models of a-Si and a-Si:H within classical molecular dynamics.
employing the empirical Tersoff interatomic potential for Si, which has been used extensively for c-Si and a-Si. All structural, electronic and optical properties of our models were calculated using structures determined from ionic relaxations using density functional theory (DFT), as implemented in the Vienna \textit{ab initio} simulation package (VASP). In chapter 4 we discuss the effect of H content on optical and mobility gaps of bulk amorphous silicon. In chapter 5 we looked at the effect of H oversaturation on optical and electronic properties. This work shows that the hydrogen incorporation is one of the crucial points to determine the electronic and optical properties of amorphous silicon. We study a-Si:H/c-Si interfaces, in chapter 6 focusing on the structural electronic and optical properties. We present for the first time first principles calculation of the band alignment properties of the a-Si:H/c-Si interfaces. In chapter 7 we discuss initial results on the structural properties of crystalline core and amorphous shell silicon nanowires and band gap modification in germanium nanowires by surface terminations. Finally the conclusions from thesis and future outlook are presented in chapter 8.
CHAPTER 2

2 Literature review

2.1 Hydrogenated Amorphous Silicon (a-Si:H)

Crystalline semiconductors are very well known, including silicon (the basis of the integrated circuits used in modern electronics)\textsuperscript{24,25,26}, Ge (the material of the first transistor)\textsuperscript{27}, GaAs and the other III-V compounds (the basis for many light emitters)\textsuperscript{28,29}, and CdS (often used as a light sensor)\textsuperscript{30}. In crystals, the atoms are arranged in near perfect, regular arrays or lattices. Of course, the lattice must be consistent with the underlying chemical bonding properties of the atoms. For example, a silicon atom forms four covalent bonds to neighbouring atoms arranged symmetrically about it. This tetrahedral configuration is perfectly maintained in the diamond lattice of crystal silicon, figure 2.1(a).

There are also many noncrystalline semiconductors. In these materials, the chemical bonding of atoms is nearly unchanged from that of crystals. Nonetheless, significant disorder in the angles between bonds eliminates the regular lattice structure. Such noncrystalline semiconductors can still show reasonable electronic properties; sufficient for many applications including field effect transistor (FET), liquid crystal display (LCD), sensors, large-area electronics and photovoltaic\textsuperscript{31,32,33,34,35,36,37,38,39,40}. Amorphous silicon (a-Si) is the paradigm noncrystalline semiconductor. It does not have the structural uniformity of crystalline silicon. Small structural deviations in this material result in defects such as “dangling bonds” where Si atoms lack a fourth neighbour to which they can bond. These defects provide sites for electrons to recombine with holes rather than contributing to electrical conduction. a-Si also shows different types of bond lengths and angles that deviate
from those of crystalline Si. Figure 2.1 (b) shows the structure of a model of amorphous silicon indicating the dangling Si with blue spheres.

Amorphous silicon is not completely disordered. The disorder in a-Si is represented by the radial distribution function (RDF). The RDF $g(r)$ is the local number density of atoms at a distance $r$ from a reference atom, averaged with respect to the choice of this atom and discussed in section 3.3.1. In figure 2.1 (c), we show the RDF of crystalline and amorphous Si. The RDF of the crystal consists of a series of sharp peaks located at the first-neighbour distance, the second-neighbour distance, and so forth.

Figure 2.1 Structural models for (a) Crystalline silicon (b) Amorphous silicon (dangling Si is indicated by blue spheres) (c) Radial distribution of crystalline and amorphous silicon.
In contrast, for amorphous silicon, the characteristic features are a number of peaks that become broader and less distinct with increasing $r$. The position of the first peak is an estimate for the average first-neighbor distance $r_1$, the position of the second peak an estimate for the average second-nearest-neighbor distance $r_2$ and so forth. Moreover, these estimates can also be used to estimate the mean Si-Si-Si bond angle (degree):

$$\theta = \arcsin\left(\frac{r_2}{r_1}\right)$$

And from the width of the first- and second-neighbor peaks, the variation in the bond angle can be estimated (under the assumption that there are no correlations between bond length variations in neighboring bonds). At larger distances, the RDF tends to a constant value, which indicates disorder.

The leading materials over the last four decades in the production of thin film solar cells are a-Si and hydrogenated a-Si. They are also considered the model amorphous covalent materials to study the rich interplay between structural disorder, chemical bonding and electronic and optical properties. Although amorphous silicon has poorer electronic properties than crystalline silicon, it offers low processing and fabrication costs, being deposited inexpensively and uniformly over a large area. It is technologically important as a cheap semiconductor material for large-area electronics and photovoltaic applications. The applications are therefore almost entirely in situations in which either a large device or a large array of devices is needed. The technology that has received the most attention is the photovoltaic solar cell - large scale power production obviously depends on the ability to cover very large areas at a low cost. Input and output devices such as displays, photocopiers and optical scanners also take advantage of the large area capability. Each of these applications requires an electronic device whose size matches the interface with human activity - either a display screen or a sheet of paper - with typical area of 25 $\text{cm}^2$ or larger.
The electronic devices are made up of a few different circuit elements, such as transistors, sensors, light emitting diodes etc.\textsuperscript{32-37, 41}. In reference\textsuperscript{31} the actual and potential applications are also discussed.

a-Si is also a model system for the study of fundamental properties of amorphous and disordered materials.\textsuperscript{39-40, 42} Despite its amorphous character, which reduces carrier mobility because disorder of the structure enhance the electron and hole scattering, the primary advantage offered by a-Si:H compared to crystalline silicon (c-Si) lies in its economically favourable production technique. Thin films of a-Si:H can be deposited over large areas using plasma enhanced chemical vapour deposition at low temperatures, allowing the use of plastic and flexible large area substrates in a cheap roll-to-roll process\textsuperscript{43}. In contrast, there are significant costs associated with depositing c-Si such as using high temperature for manufacturing, preventing use of flexible and cheap substrates.

Hydrogenation is used to improve the properties of a-Si. Hydrogen drives up device performance by passivating the dangling bonds of undercoordinated silicon atoms that introduce charge trap states in the band gap and act as very effective recombination centres\textsuperscript{14, 41}. The significantly reduced the defect density enables a fairly high carrier mobility\textsuperscript{44} and also strong photoconductivity\textsuperscript{45}, making hydrogenated amorphous silicon (a-Si:H) a useful semiconductor. Thin films made of hydrogenated a-Si are also the dominant transistor technology used for addressing pixels in common displays\textsuperscript{33}. They also compete as so-called generation II solar cells reporting efficiencies of 10.1\%\textsuperscript{46}, while nanostructured core-shell crystalline/amorphous (c-Si/a-Si:H) nanowire solar cells have been demonstrated with efficiencies of 7.29\%\textsuperscript{22} and lately up to 10.04 \%\textsuperscript{17}.

In the visible part of the solar spectrum, the absorption coefficient of a-Si:H is higher by an order of magnitude than that of c-Si\textsuperscript{47,48}. Higher absorption coefficient means that less material is required to absorb the same amount of light, thus allowing the use of thin films 1
µm thick. Although a-Si:H is a promising material for cheaper electronic devices and solar cells, there are also some fundamental disadvantages compared to c-Si. Among them, we can mention the lower carrier mobility (1-10 cm²/Vs) of a-Si:H as compared to 1000 cm²/Vs in c-Si and the well known efficiency degradation during initial exposure to sunlight. This effect is known as the Staebler Wronski Effect (SWE)\textsuperscript{16,49}, after its discoverers, Staebler and Wronski. They found that a-Si:H degrades upon light soaking and goes into a metastable state with lower dark and photo conductivities, which can be annealed back at about 200°C\textsuperscript{50}. The metastable defects are usually excess silicon dangling bonds. The saturated metastable defect density correlates with the hydrogen content and bandgap\textsuperscript{51}. Despite extensive studies the microscopic mechanisms for the Staebler-Wronski effect remain unclear. Several different mechanisms have been proposed for the SWE including breaking of weak Si-Si bonds by nonradiative recombination of carriers \textsuperscript{50,52,53}, the capture of carriers at existing charged dangling bond sites\textsuperscript{54}, the generation of pairs of dangling bond floating bond defects\textsuperscript{55}, the local metastable states of dopant atom\textsuperscript{56}, the diatomic H complex in a-Si:H and the role of H interstitials in a-Si:H\textsuperscript{57,58}. Recently, the role of vacancies and voids in the light-induced degradation process was discussed\textsuperscript{59,60,61}. The vacancy is defined as a lattice site at which up to 3 Si atoms are missing\textsuperscript{59} and recently it was postulated that the vacancies can possibly act as the precursor for the light induced dangling bond creation by the SWE. Despite extensive studies, the microscopic mechanisms for the Staebler-Wronski effect remain unclear and it is remains an active field of research for a-Si:H solar cells.

As grown a-Si is a defective amorphous material, possessing numerous low coordinated Si atoms and Si-Si bonds, and bond angles that deviate significantly from the bulk c-Si atomic geometry. A primary defect is the so-called dangling bond, which is present in a-Si when undercoordinated Si atoms are formed. Incorporation of H during a-Si:H growth, either
intentionally or not, is believed to passivate these dangling bonds and break strained or weak Si-Si bonds, both of which can reduce the concentration of these defects in the system and reduce the disorder compared to unhydrogenated a-Si\textsuperscript{41}. However, in a grown a-Si:H film, an increase in the hydrogen content can be associated with a higher degree of disorder\textsuperscript{62}. H concentration also strongly influences the fundamental optical and mobility gaps in a-Si:H\textsuperscript{63}. The importance of short and long Si-Si bonds has recently been discussed in the context of the band tail and mid-gap states in a-Si:H\textsuperscript{64,65,66,67,68,69}. Fedders et. al. study\textsuperscript{64} observed that valence tail states preferentially involved short bond lengths, whereas conduction tail states tended to be involved with longer bond lengths. Angle distortion was also mentioned but no specific relation to the band tails was detected. In addition, related work was undertaken in reference\textsuperscript{65}. In reference \textsuperscript{66} this analysis was extended to their collection of models. In agreement with these earlier reports\textsuperscript{64-65, 68}, they confirm a robust tendency for valence and conduction tail states to be associated with short and longer bonds respectively. On the other hand, they for the first time detect analogous features for the bond angle distribution, where they see that smaller and larger bond angles are correlated with valence and conduction tails respectively.

The presence of band tails and mid-gap states results in very different electronic properties of a-Si:H compared to the equivalent c-Si\textsuperscript{31,70}. The band tail states represent the energy states of electrons that are formed by the distorted bonds, angles, and bond lengths in the a-Si:H network. The width of the band tails is a measure of the degree of disorder in a-Si:H, or in any amorphous material\textsuperscript{68}. The current understanding is that valence band tail states are contributed from short Si-Si bonds and conduction band tail states come from long Si-Si bonds\textsuperscript{64-68}. In addition Khomyakov et. al.\textsuperscript{69} showed that the strained bonds (longer Si-Si bonds) significantly contribute to the mid-gap states as much as dangling bonds.
Despite the importance of a-Si and a-Si:H, a detailed microscopic understanding of the role of hydrogen incorporation into the silicon host and its effect on the optical and mobility gaps remains an outstanding challenge. The amount of hydrogen needed to passivate dangling Si and its influence on the electronic and optical properties of the amorphous network are open fundamental questions that link chemical composition and structure to continue improving the photovoltaic conversion efficiency with respect to earlier devices.

Of particular importance for a-Si and a-Si:H are the optical properties, which determine light absorption in a solar cell. However, the dependence of the optical properties on hydrogen content and disorder in a-Si:H have led to conflicting interpretations in the literature regarding the effect of hydrogenation on the optical band gap so that a consistent understanding of the influence of H content on the optical properties of a-Si:H still eludes us.

Cody et al. showed that for two different a-Si:H films with H concentrations of 9% and 13%, the same optical gap is obtained and that the fundamental determining factor is the disorder in the structure as tuned by temperature. In addition, these authors found that the optical gap will not increase beyond a maximum H concentration, since the excess H increases randomness in the film (giving a reduced optical gap). Yamasaki proposed that the optical gap of a-Si:H is affected by the bonding H-content rather than by disorder. He found that the deposition temperature affects the disorder and defect states present in the structure. Yamaguchi and Morigaki examined the optical gap of a-Si:H at deposition temperatures of 100°C and 250°C and they found that the optical gap from the 100°C deposition shows a dependence on H concentration, but from a 250°C deposition the optical gap is constant irrespective of H concentration. Daouahi et al. stated that the optical gap of a-Si:H depends on the H-content which is regulated by the H₂ concentration in the gas mix in
magnetron sputtered a-Si:H at 250 °C. Their results show a constant optical gap for hydrogen at 10%, 13% and 15% (with all other parameters held fixed), but for 6% H-content a smaller optical gap is obtained. This would appear to indicate, at the larger H concentrations, a constant optical gap in a-Si:H, although these authors do not make this finding. Kre et al. grew a-Si:H films with H₂ pressure and deposition temperature changed. They found that with increasing H concentration, the absorption edge shifts to higher energy from 1.45 eV for a-Si to 1.60 – 1.63 eV for a-Si:H samples under different H₂ pressures, which can indicate that a saturation of H-content is reached, although, similar to reference, this is not stated. The primary effect of H was proposed to be its effect on disorder through relaxation of the network. Manfredotti et al. presented PECVD grown a-Si:H with different substrate temperatures. Formation of monohydrides and dihydrides was proposed to be of importance, affecting the optical gap of a-Si:H. These authors found that after a critical total H-content, the optical gap was constant, but the expectation would be that inclusion of SiH₂ species should continuously increase the gap. Viturro and Wieser studied a-Si:H up to 8.5 % H-content, with this regime showing an increase in the optical gap. However, compared to reference and later works, e.g. references, this H-content may be too small to be saturated.

Another challenge on amorphous silicon is that the presence of a higher content of hydrogen in amorphous silicon or oversaturation of hydrogen in a-Si. The work of Maroudas et al., points out that a hypersaturation of H will generate nanoscopic regions of c-Si in an a-Si:H matrix. Additionally, in references the is a constant supply of H to a-Si:H during growth. But still it is not clear what the effect of for mild hydrogen oversaturation in amorphous silicon will be.

In this part of the thesis (Chapters 4, 5) we will address the following fundamental issues
• Detailed microscopic understanding of the role of hydrogen incorporation into the a-Si host and its effect on the optical and mobility gaps in the case of undersaturation, saturation and mild oversaturation.

• The amount of hydrogen needed to passivate dangling Si and its influence on the electronic and optical properties of the amorphous network.

• Understanding the local bonding environment of hydrogen in amorphous silicon

• The role of hydrogen on the Staebler Wronski effect

2.2 Amorphous-Crystalline silicon interface (a-Si:H/c-Si)

Heterojunctions of hydrogenated amorphous and crystalline silicon, henceforth denoted a-Si:H/c-Si, have gained much attention recently as demonstrated by the so-called thin film silicon solar cell\(^{81,82,83}\). a-Si:H/c-Si heterojunction solar cells are a high-efficiency concept based on silicon wafers, they use thin-film processing techniques and can be made using only highly abundant materials. Reaching more than 23\% conversion efficiency\(^2\), which has to be compared with the physical limit of 29\% conversion efficiency in a c-Si solar cell\(^{84}\), the process to make the cell experimentalis as follows: Starting with a clean c-Si surface, full-area coating with 10 nm of hydrogenated amorphous silicon by chemical vapour deposition suffices to create the p/n junction. The structure is then terminated with roughly 100 nm of a transparent conductive oxide (TCO) deposited by physical vapor deposition, and a screen-printed metal contact, while no structuring is required. All processing can be done around 200 °C, reducing the energy consumption in making the cells\(^{85}\). Heterojunction solar cells were first developed by Sanyo, starting research on this device structure in 1990. In 1992, 18.1\% conversion efficiency as demonstrated on 1 cm\(^2\) cell area with a heterojunction cell on an n-type silicon wafer ((n)c-Si) comprising undoped a-Si:H buffer layers ((i)a-Si:H)\(^{86,2}\). This
concept was termed 'heterojunction with intrinsic thin layer' (HIT), and successively developed further over the next 20 years. Mass production of HIT modules was launched in 1997, and until now Sanyo is the only company producing heterojunction solar cells. The independently confirmed record efficiency reported so far by Sanyo is 23.0% on 100.4 cm$^2$ with Voc = 729mV, j$\text{sc} = 39.5$ mA/cm$^2$ and FF = 80.0%, presented in 2009$^2$. In mass production, the best HIT cells have 21.6% conversion efficiency, leading to 19.0% module efficiency$^8$.

Currently most studies are devoted to a-Si:H/c-Si heterojunctions which are promising for solar applications because of the redshift in light absorption relative to crystalline Si, widely used in solar cells. However, large density of electronic states near the Fermi level in amorphous parts and at the heterointerface$^9$ and interface defects can enhance the recombination of photogenerated carriers and limit the cell efficiency. Thus, the determination and control of interface properties are a major step in the development of a-Si:H/c-Si heterojunction devices. On one hand, it has been shown that the shape of current vs. voltage (I–V) curves under illumination is sensitive to recombination at the interface$^{90, 91}$. In order to advance the application of a-Si:H/c-Si in solar cell technology, further work is needed to understand the fundamental properties of this system and the interface between amorphous and crystalline Si.

The investigation of a-Si:H/c-Si interfaces brings challenges in understanding surface orientation, the role of the interface region, the amount of hydrogen need to passivate the dangling silicon and the influence of hydrogen in electronic and optical properties, the surface stability of the interface, the band alignment between amorphous and crystalline silicon. A better understanding of these challenges will improve a-Si:H/c-Si heterojunctions because these challenges influence device performance.
In this regard first principles simulations of model a-Si:H/c-Si interfaces can play an important role. There have been some experimental and theoretical studies of a-Si/c-Si and a-Si:H/c-Si interfaces, e.g. in references \textsuperscript{92,93,94,95,96,97}. But the inaccessibility of the interface atomic structure to experimental probes and the size of systems that can be handled by simulation as well as the extent of configuration space that can be explored through calculations have placed restrictions on understanding and improving the properties of a-Si:H/c-Si heterojunctions. Despite the importance of the a-Si:H/c-Si system, there has only been one recent first principles study of a model interface by Tosolini et al.\textsuperscript{96}; these authors showed that the formation of the interface between a-Si:H and c-Si induces changes in the structural properties, but the electronic properties were not examined in detail.

2.2.1 Band offsets

Among the most important properties that determine the feasibility and performance of heterostructure devices are the band offsets (conduction and valence band offsets) and interface defects. They are key parameters that determine the band bending on each side of the device, recombination of photogenerated carriers, as well as the charge carrier transport across the interface. At the heterojunction interface, there is an energetic barrier that carriers have to overcome due to the band offsets. A schematic diagram of the band offsets of heterojunction device is shown in figure 2.2. The band gap of a-Si is approximately 1.8 eV while the band gap of c-Si is 1.12 eV. The a-Si:H/ c-Si wafer junction band bending is strong due to the difference in Fermi level and the high-doping of the a-Si layer. The strong band-bending induces an inversion layer at the surface. At the inversion location, the Fermi level is close to the valence band. The inversion layer attracts the minority carriers and repels the majority carriers; it works like an electronic junction. The electronic junction is not the actual junction between the two materials, but it is where carriers recombine. Since the electronic
juncture and the physical material interface junction are spatially separate in this case, the interface defects are low for this heterojunction structure compared to other heterojunctions because recombination is low. Moreover, the quality of the surface passivation is improved due to the inversion layer since it reduces the recombination at the material interfaces. The determination of band offsets and band lineup at the interface is thus of crucial importance. Band engineering of devices with desired properties, particularly photovoltaic devices, critically requires a precise knowledge of band offsets. However, reliable measurements and predictions of band offsets continue to be challenging despite extensive theoretical and experimental efforts. However there are not many reports on theoretical calculations of band offsets at the a-Si:H/c-Si heterojunction. We note that references 108 and 109 are not from first principles or TB simulations but are instead an analytical model.

Figure 2.2 Schematic band diagram of the a-Si:H/c-Si heterojunction. Eg, a-Si:H and Eg, c-Si are the a-Si:H and c-Si band gap energies; EF is Fermi level and the valence band. ΔEv and ΔEc are the valence and conduction band offsets.
Table 2.1 Overview of valence and conduction band offsets, $\Delta E_V$ and $\Delta E_C$, reported in literature for the a-Si:H/c-Si heterojunction interface. Measurement techniques are: IPE – internal photoemission spectroscopy; C-V – capacitance voltage measurements; SR – spectral response; CFSYS – constant final state yield spectroscopy. Theoretical modeling are: TB; tight-binding, AFORS-HET automat for simulation of heterostructures.

<table>
<thead>
<tr>
<th>$\Delta E_V$ [eV]</th>
<th>$\Delta E_C$ [eV]</th>
<th>Deposition technique</th>
<th>Measurement technique</th>
<th>References</th>
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<tr>
<td>0</td>
<td>-</td>
<td>Sputtered</td>
<td>IPE</td>
<td>98,99</td>
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<tr>
<td>0</td>
<td>-</td>
<td>PECVD</td>
<td>IPE</td>
<td>100</td>
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<td>0.20</td>
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<td>I-V</td>
<td>101</td>
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<td>PECVD</td>
<td>VFP</td>
<td>102</td>
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<td>0.01</td>
<td>ECVD</td>
<td>C-V</td>
<td>102</td>
</tr>
<tr>
<td>0.65</td>
<td>0.13</td>
<td>PECVD</td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>0.71</td>
<td>0.09</td>
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<td>IPE</td>
<td>105</td>
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<tr>
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<td>SR simulation</td>
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<td>CFSYS</td>
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<td>I-V, CV n/p and p/n</td>
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<td>-0.06</td>
<td>0.24</td>
<td>PECVD</td>
<td>IPE (p) a-Si:H</td>
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<td>PECVD</td>
<td>Coplanar conductance</td>
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<td>PECVD</td>
<td>CFSYS (p,i,n)</td>
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<tr>
<td>&gt; 0.25</td>
<td>n/f</td>
<td>PECVD</td>
<td>AFM</td>
<td>113</td>
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</table>

**Theoretical results**

| 0.32 - 0.42      | 0.08 - 0.26      | analytical calculation | 110 |
| 0.36 ± 0.05      | 0.18 ± 0.05      | analytical calculation  | 111 |
| 0.46 ± 0.05      | 0.14 ± 0.1       | AFORS-HET              | 112 |
| 0.36             | n/f              | TB                     | 109 |
While very high solar cell efficiencies have been obtained in silicon heterojunction solar cells, the detailed physics of the devices is still a matter of research. In particular, band offset values reported in literature for the a-Si:H/c-Si system are clearly very widespread as it is clear from table 2.1.

The average electrostatic potential technique\textsuperscript{114} is used to compute the band offsets of a-Si:H/c-Si interface. The bulk valence band edges are aligned through a reference potential calculated across the interface of the heterostructure. The difference in valence band maxima (VBM) of a-Si:H and c-Si is $\Delta E_{\text{VBM}}$. The discontinuity in this reference potential across the heterostructure interface is defined as $\Delta V_{\text{step}}$. The valence band offset, $\Delta E_v$, is calculated as

$$\Delta E_{v}^{aSi-cSi} = \Delta E_{v}^{aSi-cSi}_{BM} + \Delta V_{\text{step}}^{aSi-cSi}$$ \hspace{1cm} (2.1)

The conduction band offset is determined from $\Delta E_v$ and the difference in bulk band gaps, $\Delta E_g$, as

$$\Delta E_{c}^{aSi-cSi} = \Delta E_{g}^{aSi-cSi} + \Delta E_{v}^{aSi-cSi}$$ \hspace{1cm} (2.2)

According to reference\textsuperscript{113} using conductive probe atomic force microscopy measurements suggested that the valence band offset should be larger than 0.25 eV.

The performance of the heterojunction interface cell critically depends on the recombination at the a-Si: H/c-Si interface. These losses can be suppressed by a strong band bending in the crystalline wafer which leads to a lower density of defect states at the interface\textsuperscript{115}. In this part of the thesis we study the challenges of a-Si:H/c-Si interfaces such as the understanding of the stability of different surface orientations, the role of orientation and amorphous layer thickness on interface defects and band offsets, the amount of hydrogen needed to passivate...
the dangling silicon bond and the influence of hydrogen in electronic and optical properties. A better understanding will improve the quality of a-Si:H/c-Si heterojunctions and influence device performance.

2.3 Semiconductor nanowires

The motivation to manipulate matter on the nanometre scale arises not only from the fascinating emergence of novel behaviours at small length-scales, but also from the appeal of engineering material properties by building up from the nanoscale. A true nanotechnology based on materials built from the bottom up will require parallel and scalable means of fabrication. While several efforts in nanomaterials research may in time realize these goals, here we focus on semiconductor nanowires. Semiconductor nanowires are defined as free-standing semiconductor structures with diameters of a few to tens of nanometres with lengths of tens of nanometres to tens of microns. The operating principles and performance of these devices are intimately related to functional interfaces and heterostructures within the devices\textsuperscript{116}. The functions performed by heterointerfaces include passivation, electrical isolation, charge transfer and internal field generation. Exquisite control over the composition and perfection of interfaces is required for the successful fabrication of high performance planar devices, and is expected to be equally important in nanoscale devices given the inherently large surface area to volume ratios. The demonstration of lasing in core–shell semiconductor nanocrystals grown in solution provides an excellent example of the importance and utility of interface control in nanoscale materials\textsuperscript{117}.

2.3.1 Amorphous Core/crystalline shell Silicon Nanowires

Silicon nanowires (SiNWs) have been proposed to be used as sensors\textsuperscript{118,119,120} and field effect transistors\textsuperscript{121,122,123}. Moreover, SiNWs find applications more and more in the energy chain, either for energy storage as efficient batteries\textsuperscript{124} or as energy harvesting devices like thermal
electrical generators\textsuperscript{125,126} and most importantly as solar cells\textsuperscript{20,127}. Nanowire-based solar cells are very promising for the third generation low-cost highly efficient light harvesting devices. Two types of nanowire-based solar cells, i.e., with axial or radial p-n junction, are under intensive investigation. An issue of the axial p-n junction configuration is that the surface is greatly enlarged. To keep surface recombination acceptable, one should passivate the p- as well as the n-type region, which is difficult in practice. The radial p-n junction configuration relies on a core–shell structure. Because of the small diameters of the nanowires, most of the core region is depleted from majority carriers so that the electron–hole pairs generated can be immediately separated by the electrical field by drift so that the recombination in the crystalline silicon (c-Si) cores is very low. As a consequence, materials with rather low minority carrier lifetimes could be tolerated to fabricate solar cells with efficiencies comparable with those of costly monocrystalline counterparts\textsuperscript{20}. Furthermore, a densely packed nanowire array provides antireflection properties at the surface and light trapping within the arrays. Light absorption is greatly enhanced within a nanowire carpet only several micrometers thick, so that highly efficient thin film solar cells could be realized by using silicon nanowires.

However, even if light absorption is greatly enhanced, efficiencies of SiNW-based solar cells are still very low\textsuperscript{21, 128}. Only one group reported an efficiency above 10\%\textsuperscript{129}. However, highly sophisticated technologies have been used in their experiment. Our experimental collaborator in The Institute of Photonic Technology (IPHT) Jena, Germany from Prof. Fritz Falk’s group presented a low-cost process for SiNW solar cell preparation resulting in an efficiency slightly above 10\%\textsuperscript{18}.

Core-shell a-Si/c-Si nanowires is an active and emerging research field. Understanding of the physical properties of a-Si/c-Si core-shell nanostructures is expected to play an important role
improving the device performance. However, the available knowledge about the fundamentals of this field is currently quite poor, particularly because their experimental characterization remains a challenging task. In such a situation atomistic simulations may represent an alternative to bypass experimental difficulties. In this chapter 6 we have studied the following issues.

- Generation of structural models of different amorphous layer thickness a-Si/c-Si core-shell nanowires.
- Structural characterization of and different amorphous layer thickness a-Si/c-Si core-shell nanowires.
- Initial results of electronic and optical properties of a-Si/c-Si and a-S:H/c-Si core-shell nanowires.

2.3.2 Germanium Nanowires

Germanium (Ge) nanowires are of great interest because of their unique electronic and optical properties that result from their low dimensionality and the well-known quantum confinement effect. While silicon (Si) nanowires have tended to dominate in this area, interest in other materials such as germanium nanowires is growing. Germanium nanowires can be used in high quality field effect transistors (FET), sensor applications and in solar cells due to their higher electron and hole mobility and lower band gap compared to Si. The intrinsic characteristics of Ge nanowires such as one dimensionality, high surface-to-volume ratio, biocompatibility, as well as the tuneable band gap make them a unique and special class of semiconductors.

From the perspective of modifying the band gap of nanowires, the focus for both Si and Ge nanowires has been on exploiting the quantum confinement
effect for H-terminated nanowires. Reference\textsuperscript{141}, investigated the electronic structure of SiNWs with different diameters and surface coverage H, Br, Cl, and I. They concluded that the origin of band gap reduction comes from the surface species weakly interacting with the SiNW and they also address that due to the formation of surface states associated with halogen binding, the band gap was found to increase in the order of Cl < Br < I. It was previously shown, using density functional theory (DFT) calculations, that the band gap of small diameter Si nanowires can be tuned by up to 1 eV by changing the nature of the nanowire surface terminating group, from -H to –NH\textsubscript{2} or –OH\textsuperscript{139}. Since then, there have been a number of papers focussing on the effect of the surface terminating group in Si nanowires\textsuperscript{131,142,143}. In reference\textsuperscript{142} studies found that the magnitude of the band gap reduction in –OH-terminated Si nanowires was surface-facet dependent and reference\textsuperscript{143} also investigated that 50\% of H-terminations on a (100) Si nanowire are substituted for –OH or –F atoms, the band gap was predicted to change from a direct to indirect. Reference\textsuperscript{144} showed the band gap narrowing of SiNWs can be achieved by changing surface passivation from H to OH and correlated the reduction to the electronegativity of the passivating species.

By contrast, for Ge nanowires, the focus has been on the effect of quantum confinement in H-terminated nanowires. In references\textsuperscript{131,145,146,147} H terminated Ge nanowires bandgap increases with decreasing diameter, due to quantum confinement. The influence of functional groups such as halogens\textsuperscript{137,148,149}, SH\textsuperscript{150} alkenes, and alkyne\textsuperscript{137,150,151} were studied. Reference\textsuperscript{149} showed that (100) GeNWs, the band gaps are reduced with F and Cl surface passivations as compared to that of H passivation. References\textsuperscript{137,150,151} studied experimentally how to prevent the problems of oxidation and hysteresis in electric current of GeNWs. Reference\textsuperscript{152} studied the effect of surface defects (which act as charge traps) on electronic properties of the 100\% (100) OH-GeNW. The calculated band gap and effective mass of electrons of the
100% (100) OH-GeNW with surface trap state defects. They find that the presence of charge traps in OH-GeNWs decrease the band gap of OH-GeNWs and vary the effective mass of electrons. Perhaps surprisingly, there have been no studies of the optical properties and band gap modification of H, -OH, NH₂ surface terminating of different diameters of GeNWs. In this part of the thesis we have studied optical properties and bandgap modification of H, -OH, NH₂ surface termination of different diameters of GeNWs.
CHAPTER 3

3 Theoretical Background, Methodology and Preparation of a-Si

3.1 Molecular Dynamics and Interatomic Potentials

With the rise of bulk and nanotechnological applications, the industrial demand and scientific interest in understanding the microscopic properties of a-Si:H has seen a vast and rapid increase over the last four decades. While experiments are valuable in gaining understanding of the structural properties a-Si:H, they are often not suitable to study what happens on a microscopic level. Simulations can lead to insights that can sometimes not be extracted from experimental measurements. This is enhancing our understanding of materials.

Classical Molecular dynamics (MD) is the method we use to generate and understand the structural behaviour of a-Si:H. In this thesis, the technique of classical MD simulation\textsuperscript{152a, 152b}, has been applied to generate and study a-Si:H, interfaces between a-Si:H/c-Si, and core-shell a-Si:H/c-Si nanowires. This section will give a basic introduction to the equations that the method of MD relies on. MD is a computer simulation technique where the time evolution of a set of interacting particles is followed by integrating their equation of motion. The technique has been applied to systems of several hundreds to millions of particles and has given much insight into the behaviour of interacting classical many-particle systems. The physical movements of atoms and molecules are investigated by numerically solving Newton’s equation of motion using a description for the inter-atomic interaction that ignores the electrons and studies atoms and bonds as a ball and spring model.

\[
\vec{F}_i = m_i \ddot{\vec{r}}_i = m_i \frac{d^2}{dt^2} \vec{r}_i(t) \quad i = 1, 2, 3...N
\]
where \( m_i \) is the mass of particle \( i \), \( r_i(t) \) its position at time \( t \), \( F_i \) the force acting on particle \( i \), and \( N \) the number of particles. The force on a particle, \( \vec{F}_i \) (the left hand side) can be obtained from taking the derivative of the potential energy \( U \), with respect to position.

\[
\vec{F}_i = -\frac{dU}{d\vec{r}_i}, \tag{3.2}
\]

where \( U \) is the potential energy. When the form of \( U \) is analytical (such as with potentials), calculating the forces on an atom is relatively easy. Thus, we can solve for accelerations, \( \ddot{a}_i \) because the masses of the atoms are known. We can integrate the accelerations to obtain velocities, and integrate velocities to obtain positions.

### 3.1.1 Verlet leap-frog algorithm

In practice, all integrations are carried out numerically. The parameter that controls the fineness of the integration is called the timestep, \( \delta t \). Knowing positions, velocities, and accelerations at time \( t \), we can integrate to obtain positions, velocities, and accelerations at time \( t + \delta t \).

Once the acceleration of each particle is known, an integrator is used to evolve the position and velocity of each of the particles in the system by one time step. One of the most popular integrators, which is also the integrator used by the GULP code in this thesis, is the Verlet\(^{153}\) leapfrog algorithm given by:

\[
\vec{r}(t + \delta t) = \vec{r}(t) + \delta t \vec{v} \left( t + \frac{1}{2} \delta t \right) \tag{3.3}
\]

\[
\vec{v} \left( t + \frac{1}{2} \delta t \right) = \vec{v} \left( t - \frac{1}{2} \delta t \right) + \delta t \ddot{a}(t) \tag{3.4}
\]
Where \( r \) is the position, and \( v \) is the velocity, \( a \) is the acceleration, \( t \) is the time, and \( \delta t \) is the timestep. The name “leapfrog” comes from the fact that the positions and velocities are calculated at staggered time steps, so the positions and velocities appear to “leapfrog” over each other. These are fairly easy to evaluate, so most of the computational time from an MD simulation is spent in the evaluation of forces. Since the configurational force on a single particle depends on the position of every other particle in the system, evaluating this force can be computationally very expensive especially as the complexity of the potential is increased.

3.1.2 **Interatomic Potentials**

In MD methods we use a potential function \( U \) to describe interaction among atoms. In this thesis we use the potential due to Tersoff to describe the atom-atom interactions in silicon. The Tersoff interatomic potential was proposed in 1986 with the intent to develop a potential with which it was feasible to calculate the structure and energetics of complex covalently bonded systems (e.g. amorphous silicon\(^{154,155,156}\)). The potential format that Tersoff proposed was motivated by ideas about the dependence of bond order upon the local environment. The Tersoff potential represents the first such potential to incorporate the bond order in the functional form, albeit empirically. The great advantage of empirical methods is the reduced calculation effort but the number of simulated properties can be limited by the functional form of the potential itself or it depends on the parameterization\(^{154}\). The Tersoff potential is modelled by a Morse-type pair potential, which allows a physical interpretation of the potential parameters\(^{154-156}\). Tersoff continued to make minor adjustments to the functional format\(^{154-156}\); the format employed in this research and presented here is that published in references\(^{156,157}\).
system, \( U \), could be captured as the sum of the energy of the individual bonds in the system. The Tersoff potential \(^{156}\) represents this empirically with:

\[
U = \frac{1}{2} \sum_{i \neq j} f_c(r_{ij}) \left[ f_R(r_{ij}) + b_{ij} f_A(r_{ij}) \right] \tag{3.5}
\]

The function \( f_c \) is a cutoff function designed to restrict the range of the potential. The first term in square brackets in Eq. 3.5 is interpreted to represent the repulsive electrostatic force that two atoms encounter when brought within close proximity to each other. The second term is interpreted to represent the bonding energy between two atoms. This term is adjusted by \( b_{ij} \) which includes considerations of the bond order and the local environment.

\( f_A \) and \( f_R \) to have the form:

\[
f_A \left( r_{ij} \right) = A_{ij} \cdot \exp(-\lambda_{ij} r_{ij}) \tag{3.6}
\]

\[
f_R \left( r_{ij} \right) = B_{ij} \cdot \exp(-\mu_{ij} r_{ij}) \tag{3.7}
\]

where \( A_{ij} \) and \( B_{ij} \) are the geometric averages of the fitted parameters \( A \) and \( B \) for atoms \( i \) and \( j \). The parameters \( \lambda_{ij} \) and \( \mu_{ij} \) are the averages of the fitted parameters \( \lambda_a \) and \( \mu_a \) for atoms \( i \) and \( j \).

The function \( b_{ij} \) represents the only deviation from a potential that is otherwise wholly pairwise\(^{154-157}\). It represents a measure of the interatomic bond order and has been written:

\[
b_{ij} = \chi_{ij} \cdot (1 + \beta_i^{ni} \cdot \xi_i^{ni})^{\frac{-1}{2m}} \tag{3.8}
\]

\[
\xi_{ij} = \sum_{k \neq i,j} f_c(r_{ij}) \cdot \omega_{ik} \cdot g(\theta_{ijk}) \tag{3.9}
\]
where $\theta_{ijk}$ is the bond angle between bonds $ij$ and $ik$. The parameter $\chi_{ij}$ has a value of unity if between two atoms of the same type, for a bond between silicon and hydrogen this term has a value of 1.00. Similarly the parameter $\omega_{ij}$ also has a value of unity, and was included in the potential for possible future flexibility. The parameters $\beta$, $n$, $c$, $d$, and $h$ are all dependent only on atom $i$.

The Tersoff functional format includes an explicit cutoff term\textsuperscript{154-158}. This step function is designed to create a smooth transition to between the separation ranges of $R$ and $S$. The parameters $R$ and $S$ are chosen as to include the first-neighbour shell only for selected structure.

\begin{equation}
\begin{align*}
    g(\theta_{ijk}) &= 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos(\theta_{ijk}))^2} \\
    \theta_{ijk} &< \theta_{ij} < \theta_{kk} \\
    \theta_{ij} &< \theta_{ik} < \theta_{jk} \quad (3.10)
\end{align*}
\end{equation}

\begin{equation}
\begin{align*}
    f_c (r_{ij}) &= \frac{1}{2} + \frac{1}{2} \cdot \cos \left( \pi \cdot \frac{r_{ij}-R_{ij}}{S_{ij}-R_{ij}} \right) \quad R_{ij} < r_{ij} < S_{ij} \\
    r_{ij} &< R_{ij} \quad (3.11)
\end{align*}
\end{equation}

Table 3.1 show parameters for all the interactions. The parameters for the Si–Si and Si–H, and H–H interaction can be computed by combining the parameters for Si and H in the way developed by Tersoff. Here the parameters $R$ and $S$ for the hydrogen interactions were not obtained arbitrarily during the fitting procedure. They were chosen such that the cut-off function falls.

Table 3.1 Parameters for silicon and germanium for the Tersoff potential.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Si</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (eV)</td>
<td>1830.8</td>
<td>86.7120</td>
</tr>
<tr>
<td>B (eV)</td>
<td>417.18</td>
<td>43.5310</td>
</tr>
<tr>
<td>λ (1/Å)</td>
<td>2.4799</td>
<td>3.7879</td>
</tr>
<tr>
<td>μ (1/Å)</td>
<td>1.7322</td>
<td>1.9800</td>
</tr>
<tr>
<td>β</td>
<td>1.1 x 10^-6</td>
<td>4.0000</td>
</tr>
<tr>
<td>n</td>
<td>0.78734</td>
<td>1.00</td>
</tr>
<tr>
<td>c</td>
<td>1.0039 x 10^-5</td>
<td>0.00</td>
</tr>
<tr>
<td>d</td>
<td>16.217</td>
<td>1.00</td>
</tr>
<tr>
<td>h</td>
<td>-0.59825</td>
<td>1.00</td>
</tr>
<tr>
<td>R (Å)</td>
<td>2.7</td>
<td>0.80</td>
</tr>
<tr>
<td>S (Å)</td>
<td>3.0</td>
<td>1.00</td>
</tr>
</tbody>
</table>

3.1.3 Ensembles

MDs simulations generate information at the microscopic level including the atomic positions and velocities. The conversion of this microscopic information to macroscopic observables such as pressure, energy, temperature etc., requires statistical mechanics. Through MD, macroscopic properties of a system are explored through molecular simulations like examining the mechanics and energetics of conformational change.

In MD, we often encounter limitations and inconsistencies which arise from the use of the micro-canonical ensemble that corresponds to simulations at constant energy, number of particles and volume. In particular, ordinary laboratory experiments are carried out at
constant temperature and constant pressure but many molecular dynamics simulations are
done at constant energy and volume. However, the temperature $T$ can be related to the
average of the kinetic energy:

$$\frac{\sum_{i=1}^{n} p_i^2}{2m_i} = \frac{3}{2} N k_B T$$

where $T$ is the temperature, $N$ is the number of particles and $k_B$ is the Boltzmann constant.

Each value of the energy $E$ in the microcanonical ensemble corresponds to a different
temperature and so to calculate the dynamics of the system at a given temperature, the energy
needs to be set correctly. To set the temperature conveniently, we need to take into account
the interaction of a system with the outside world at a temperature $T$.

In conventional constant-energy molecular dynamics, the temperature can only be obtained
after carrying out the simulations and calculating the average kinetic energy. To resolve this
situation, constant energy and constant volume (NVE) simulation methods have been
developed.

### 3.2 Density functional theory

Density functional theory is one of the successful approaches to calculate the ground state
energy of amorphous and crystalline materials. The original formulation of the DFT tells us
that the energy of a system can be exactly expressed as a functional of the one-electron
density, $\rho$. Formally, there exists a functional $E[\rho]$ that determines the ground-state molecular
electronic energy. Unfortunately, this universal functional is not known. Obviously, the goal
is to obtain a good approximation of the universal functional to be applied to any one-
electron density.
In principle, since the energy can be extracted from the one electron-density, there is no need to introduce the molecular orbital approximation in the DFT methodology. However, in the most successful DFT methodology the MD approximation is introduced by Hohenberg-Kohn\textsuperscript{160} and Kohn-Sham\textsuperscript{161}.

In DFT, the total electronic energy is expressed as a functional of the density $E[\rho]$. This functional can be written as a sum of several terms: The kinetic energy of electrons, $T[\rho]$, the energy of electrons in the external field, $V[\rho]$, and the energy of electron-electron interaction, $Vee[\rho]$,

$$E[\rho] = T[\rho] + V[\rho] + Vee[\rho] \tag{3.13}$$

Of these terms, only $V[\rho]$ is known as an explicit functional of the density,

$$V[\rho] = \int v(r)\rho(r) \, dr \tag{3.14}$$

where $v(r)$ is a multiplicative external potential acting on the electrons. For atoms, molecules and solids, $v(r)$ is simply the Coulombic potential of the nuclei with charges $Z_A$ at positions $R_A$,

$$v(r) = -\sum_A Z_A \frac{1}{|r-R_A|} \tag{3.15}$$

Using Eq. (3.8), the total energy functional of Eq. (3.12) can be expressed as

$$E[\rho] = F[\rho] + \int v(r)\rho(r) \, dr \tag{3.16}$$

where the functional $F[\rho] = T[\rho] + Vee[\rho]$. The leading contribution to the term $Vee[\rho]$ is the classical Coulomb electron-electron repulsion

$$U[\rho] = \frac{1}{2} \int dr \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr' \tag{3.17}$$
Using Eq. (3.13), the functional $F[\rho]$ may be rewritten as

$$F[\rho] = T[\rho] + U[\rho] + \text{non-classical term} \quad 3.18$$

where the non-classical term describes the quantum-mechanical effects of electronic exchange and correlation. The functional $F[\rho]$ is universal in that it is the same for any chemical system. All system-specific information is contained in the external potential $v(r)$, provided that the number of electrons $N$ is fixed.

Hohenberg and Kohn also proved\textsuperscript{160} that the total energy functional $E[\rho]$ of Eq. (3.15) is variational, that is, any trial $N$-electron density $\rho'$ gives an energy that is above the exact ground-state energy $E_0$, or $E[\rho'] \geq E_0$. Therefore, the trial density that minimizes the value of the functional $E[\rho]$ is the true ground-state density. In order to make this result practical, we need to know the functional $F[\rho]$.

3.2.1 **Kohn–Sham method**

The crucial part of the functional $F[\rho]$ is the electron-electron interaction energy $V_{ee}[\rho]$. Suppose we want to apply the Hohenberg–Kohn theory to a system of non-interacting electrons moving in the field of an external potential $v(r)$. For this system the functional is denoted by a subscript ks. The many-electron Schrödinger equation can be solved exactly; the solution is an antisymmetrized product of orbitals $\varphi_i$ determined from the single-particle Schrödinger equations.

$$\left[-\frac{1}{2} \nabla^2 + v(r)\right] \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad 3.19$$

Because the electrons in this fictitious system do not interact, the term $V_{ee}[\rho]$ vanishes, so the functional $F_{ks}[\rho]$ becomes simply
\[ F_{ks}[\rho] = -\frac{1}{2} \sum_{i=1}^{n} |\nabla^2 | \psi_i \rangle \equiv T_{ks}[\rho] \] 3.20

with the electron density given by

\[ \rho(r) = \sum_{i=1}^{n} |\psi_i(r)|^2 \] 3.21

Formally, \( T_s[\rho] \) is a functional of the orbitals \( \psi_i \). However, for non-interacting systems, \( T_{ks}[\rho] = F_{ks}[\rho] \), which means that \( T_{ks}[\rho] \) is a universal functional of the density \( \rho \) alone. For the real (interacting) system, the functional \( F[\rho] \) can now be written as

\[ F[\rho] = T_{ks}[\rho] + U[\rho] + E_{xc}[\rho] \] 3.22

where the term \( E_{xc}[\rho] \) includes the effects of exchange and correlation. The functional \( E_{xc}[\rho] \) is unknown; formally, it is defined as \( E_{xc}[\rho] = F[\rho] - T_{ks}[\rho] - U[\rho] \). Minimization of the total energy functional

\[ E[\rho] = T_{ks}[\rho] + \int v(r) \rho(r) \, dr + \frac{1}{2} \int dr \int \frac{\rho(r) \rho(r)}{|r-r'|} \, dr + E_{xc}[\rho] \] 3.23

with respect to \( \rho \) yields a set of one-electron Hartree-like equations known as the Kohn–Sham equations

\[ \left[ -\frac{1}{2} \nabla^2 + v(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \] 3.24

The Kohn–Sham potential \( v_{ks}(r) \) is the effective potential energy operator defined as a functional derivative of the functional \( E[\rho] - T_{ks}[\rho] \). It can be written as

\[ v_{ks}(r) = v(r) + v_{xc}(r) + v_H(r) \] 3.25
where \( v \) is the potential of the nuclei and \( v_H \) is the effective electronic Hartree potential, and \( V_{XC} \) is exchange-correlation potential. The Hartree potential \( V_H \) is the functional derivative of the electrostatic repulsion functional \( U[\rho] \)

\[
v [\rho] = \int dr \int \frac{\rho(r')}{|r-r'|} dr'
\]

and the exchange-correlation potential \( v_{xc} \) is the functional derivative of the exchange-correlation function \( E_{XC}[\rho] \)

\[
v_{xc}(r) = \frac{\delta E_{XC}[\rho]}{\delta \rho(r)}
\]

The expression of the exchange-correlation functional is the key point in a DFT calculation. There is a wide number of functionals for the exchange and for the correlation counterparts that can be chosen in a rather arbitrary way. There are basically two families of functionals for the exchange-correlation energy: the ones based on the Local Density Approximation (LDA)\(^{161}\) or including gradient corrections, like the Generalized Gradient Approximation (GGA)\(^{162}\). In the local density approximation (LDA), the value of \( E_{xc}[\rho] \) is approximated by the exchange-correlation energy of an electron in an homogeneous electron gas of the same density \( \rho(r) \)

\[
E_{xc}^{LDA}(\rho(r)) = \int \epsilon_{xc}(\rho(r)) \rho(r) dr
\]

The LDA is often surprisingly accurate and for systems with slowly varying charge densities generally gives very good results. The failings of the LDA are now well established: it has a tendency to favour more homogeneous systems and over-binds molecules and solids. In weakly bonded systems these errors are exaggerated and bond lengths are too short. In good systems where the LDA works well, often those mostly consisting of sp bonds, geometries
are good and bond lengths and angles are accurate to within a few percent. Quantities such as the dielectric and piezoelectric constant are approximately 10% too large.

Despite the remarkable success of the LDA, its limitations mean that care must be taken in its application. For systems where the density varies slowly, the LDA tends to perform well, and chemical trends are well reproduced. In strongly correlated systems where an independent particle picture breaks down, the LDA is very inaccurate. The transition metal oxides XO (X=Fe,Mn,Ni) are all Mott insulators, but the LDA predicts that they are either semiconductors or metals.

An obvious approach to improving the LDA is to include gradient corrections, by making $E_{xc}[\rho]$ a functional of the density and its gradient; which is why it is called generalised gradient approximation.

$$E_{xc}^{GA}(\rho(r)) = E_{xc}^{LDA} + \int F_{xc} \left| \nabla \rho(r) \right| dr$$

where $F_{xc}$ is a correction chosen to satisfy one or several known limits for $E_{xc}$

Clearly, there is no unique recipe for $F_{xc}$, and several dozen functionals have been proposed in the literature. They do not always represent a systematic improvement over the LDA and results must be carefully compared against experiment. The development of improved functionals is currently a very active area of research and many incremental improvements are proposed.

Comparison between Eqs. (3.16) and (3.21) suggests the following interpretation of the potential $v_{ks}(r)$: It is the external potential of a fictitious system of non-interacting electrons that has the same density $\rho(r)$ as the real (interacting) system. The density constructed from the orbitals obtained by solving the Kohn–Sham equations is the density that minimizes the
The total energy functional $E[\rho]$ of the system of interacting electrons. But the potential $v_{ks}$ itself depends on the electron density, so the Kohn–Sham equations need to be solved iteratively.

The self-consistent procedure involves the following steps:

1. **Initial Guess**
   \[ \rho(r) \]

2. **Calculate Effective Potential**
   \[ v_{\text{eff}}(r) = V_{\text{en}}(r) + \int \frac{\rho(r')}{|r-r'|} \, dr' + V_{\text{xc}}[\rho(r)] \]

3. **Solve Kohn–Sham Equations**
   \[ \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}} \right] \psi_i = \epsilon_i \psi_i \]

4. **Evaluate the Electron Density & Total Energy**
   \[ \rho(r) = \sum_i |\psi_i(r)|^2 \quad \Rightarrow \quad E_{\text{tot}}[\rho(r)] = \ldots \]

5. **Converged?**

6. **Output Quantities**
   \[ \rho_0(r), E_i[\rho_0(r)] \rightarrow \text{Forces, Eigenvalues, …} \]

![Figure 3.1 Self-consistent Iterative Solution of Kohn-Sham equations.](image)

### 3.3 Structural characterization

#### 3.3.1 Radial distribution function (RDF)

A good way to measure local structure is the radial distribution function (RDF), since it is experimentally measurable and provides an important tool for comparing the computationally created structures with the real ones. The density function $g(r)$ is defined to be the average
number density of atoms at a distance $r$ from any other atom. This function is zero at small $r$ values as at small distances atoms experience a strong repulsion. In amorphous materials there is a sharp peak at the nearest neighbour distance, followed by broader peaks at the next nearest neighbour distances. In crystals, where there is long-range order, there are only sharp peaks.

Within statistical approach, the structure of a simple amorphous system is characterised by a set of distribution functions, the simplest of these is the radial distribution function (RDF),

$$g(r) = \frac{1}{n(n-1)} dR_1 dR_2 dR_3 \ldots dR_n \sum_{i,j} \delta(|R_i - R_j| - 1)$$

This function gives the probability of finding a pair of atoms at a distance $r$ apart.

### 3.3.2 Vibrational Density of States (VDOS)

Atomic vibrations in a solid have a profound effect on its properties. For example, heat is transported via atomic vibrations and the specific heat of a material is determined mostly by the spectrum of allowed vibrational modes. Furthermore, under certain conditions, electromagnetic radiation can interact with atomic vibrations (for example in Raman scattering), thereby directly determining the optical properties of the material. In crystals, vibrational modes can be classified in terms of the wavevector because of lattice periodicity\textsuperscript{163}. This gives rise to a number of dispersion relations which describe the dependence of the vibrational frequency on the wavevector. For amorphous solids this classification is not possible\textsuperscript{164}. Vibrations in this case are usually described in terms of the vibrational density of states. Vibrational density of states (or Phonon density of states) describes the number of phonon modes of a selected frequency $\omega_i$ in a given frequency interval, if the density of wave vectors $k$ in the Brillouin zone is homogeneously distributed. The integral over the Brillouin
zone goes over all $3N$ phonon bands, where $N$ is the number of atoms in the cell. There are two popular conventions regarding normalization of the phonon DOS. Either it can be normalized to unity or to the total number of vibrational modes, $3N$.

To investigate the vibrational properties of a-Si and a-Si:H we compute the phonon density of states (VDOS):

$$VDOS = \frac{1}{3N} \sum_{i=1}^{3N} \delta(\omega - \omega_i)$$ \hspace{1cm} (3.31)

where $\omega_i \ i = 1, 2, 3... 3N$ are the phonon frequencies.

The partial (or projected) phonon density of states is determined as a contribution from the given atom to the total phonon DOS. This is a useful concept that allows one to understand the nature of various branches in the phonon spectrum.

3.4 Electronic structure

One of the fundamental properties of a semiconductor or insulator is the presence of a band gap separating the occupied valence band from the empty conduction band states. According to the free electron theory, the band gap is a consequence of the periodicity of the crystalline lattice. In the past, there was considerable debate over the reason that amorphous semiconductors had a band gap at all, let alone one that is similar to that in the corresponding crystal. Subsequent work explained that the band gap is equivalently described by the splitting of the bonding (or lone pair) and anti-bonding states of the covalent bond. The bands are most strongly influenced by the short range order, which is the same in amorphous and crystalline silicon and the absence of periodicity is a small perturbation.$^{31}$
3.4.1 **Density of states of amorphous silicon**

The electron and hole wavefunctions that extend over the whole structure are characteristic for energy states in which the charge carriers can be considered as free carriers. These states are non-localized and are called extended states. The wavefunctions of the tail and defect states are however localized in a small region of the structure and therefore these states are called localized states. It is difficult to identify an energy gap in the presence of coordination defects, since the effect of coordination defects on the electronic structure is to fill the gap with localized states whose energy is near the Fermi level, as discussed in References \(^{31, 165}\).

![Diagram of density of states for single crystal silicon and hydrogenated amorphous silicon](image)

(a) Single crystal silicon, (b) Hydrogenated amorphous silicon.

Figure 3.2 The schematic representation of the distribution of density of allowed energy states for electrons for (a) single crystal silicon (b) a-Si:H.

The density of states refers to the number of quantum states per unit energy. In other words, the density of states, denoted by \(g(E)\), indicates how densely packed quantum states in a particular system. The density of states as a function of energy is...
\[ g(k)dE = \frac{a^3}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} dE \]

The difference in the atomic structure between single crystal silicon and a-Si:H leads to the different distributions of density of allowed energy states as schematically illustrated in Figure 3.2. The periodic atomic structure of single crystal silicon results in the ranges of allowed energy states for electrons that are called energy bands and the excluded energy ranges, forbidden gaps or band gaps. Figure 3.2a shows schematically the distribution of the density of states for single crystal silicon, in which the valence band and the conduction band are separated by a well-defined band gap, \( E_g \). At room temperature single crystal silicon has a band gap of 1.1 eV. In case of an ideal crystal, there are no allowed energy states in the band gap.

As figure 3.2b demonstrates, in case of a-Si:H, there is a continuous distribution of the density of states and no well defined band gap (in the sense of the preceding discussion) exists between the valence band and the conduction band. Due to the long range disorder in the atomic structure of a-Si:H, the energy states of the valence band and the conduction bands spread into the band gap and form regions that are called band tail states; these are well known for disordered systems in general. The band tail states represent the energy states of electrons that form the distorted bond lengths and angles in the a-Si:H network. The width of the band tails is a measure of the degree of disorder in a-Si:H, or in any amorphous material—more disorder in a-Si:H means that the band tails are broader. In addition, the dangling bonds introduced by formation of an amorphous, defective structure during the melt and quench and PECVD process, result in formation of new energy states (defect states) that are indicated in green in figure 3.2b.
The wavefunctions of the tail and defect states are localized within the structure and therefore these states are called *localised states*. Consequently, mobility that characterises transport of carriers through the localised states in *a*-Si:H is used to define its band gap. This band gap is denoted by the term *mobility gap*, \( E_{\text{mob}} \), because the presence of a considerable density of states in this gap conflicts with the classical concept of the band gap (energy gap). The energy levels that separate the extended states from the localised states in *a*-Si:H are called the valence band and the conduction band mobility edges. The mobility gap of *a*-Si:H is larger than the band gap of single crystal silicon and has a typical value of 17-1.8 eV\(^{166}\). The localised tail and dangling bond states have a large effect on the electronic properties of *a*-Si:H. The tail states act as trapping centres and build up a space charge in a device, the dangling bond states act as very effective recombination centres and affect in particular the lifetime of the charge carries.

### 3.4.2 Mobility Gap

To investigate how the electronic properties and mobility gaps evolve with composition in *a*-Si:H, we investigate the nature of wavefunctions and their respective contributions to the density of states (DOS).

To quantitatively probe electron localization around the mobility edges we calculate the inverse participation ratio (IPR)\(^{51}\), of the wavefunction of each energy eigenstate \( \Psi_i(\vec{r}) \)

\[
IPR_i = V \frac{\int_V \left| \Psi_i(\vec{r}) \right|^4 d\vec{r}}{\left[ \int_V \left| \Psi_i(\vec{r}) \right|^2 d\vec{r} \right]^2}
\]  \hspace{1cm} (3.33)

Where \( V \) is the supercell volume. The IPR indicates the various topological and chemical defects present in the structural models, since the larger the IPR for an electronic state the
more spatially localised it is. In general, the localised states have higher IPR and the extended states have lower IPR.

### 3.4.3 Optical properties

The optical properties of a-Si:H are characterised by the *optical band gap*, which is important for solar cell applications since it is the fundamental quantity that characterises light absorption in the material. From the measured dielectric function, the optical band gap is determined from a Tauc plot\(^{167}\), in which we extrapolate the linear part of the function \([\alpha(E)E]^{1/2}\) plotted against the photon energy \(E\). Here \(\alpha(E)\) is the absorption coefficient which is calculated from

\[
\alpha = \frac{2\kappa\pi}{\lambda}
\]

Where \(\lambda\) is the free space wavelength of light and \(\kappa\) is the extinction coefficient. The expression for \(\kappa\) reads

\[
\kappa = \frac{1}{\sqrt{2}} \sqrt{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}}
\]

The variables \(\varepsilon_1\) and \(\varepsilon_2\) represent respectively the real and imaginary part of the dielectric function of each a-Si:H structure, calculated using the VASP post-processing routines of Furthmueller\(^{168}\).

### 3.5 Methodology

We employ a heat and quench approach to generate models of a-Si and a-Si:H using the classical molecular dynamics (MD) code GULP\(^{169}\) using the Tersoff interatomic potential for Si, which has been used extensively for c-Si and a-Si\(^{154-155,157}\). Various structural models have been proposed for a-Si\(^{170,171}\) and the interplay between experiment and theoretical...
predictions regarding structure continues to be an intriguing and still controversial topic for the physics of amorphous solids\textsuperscript{31}. The continuous random network (CRN) model\textsuperscript{170}, where every atom is four-fold coordinated\textsuperscript{172} and bond angles are distorted, has been frequently employed. There is, however, no clear explanation for this assumption beyond chemical intuition. In fact, experiments on pure a-Si yield an average coordination number of 3.88 (compared to 4 for c-Si)\textsuperscript{172} and a non-vanishing density of states in the band gap, consistent with the presence of undercoordinated Si atoms. Simulations that attempt a more realistic description of the energetics of bonding in a-Si and a-Si:H are generated from a heat and quench approach, in which c-Si is melted and quickly quenched, and typically display coordination defects, in particular three and five fold coordinated Si, that is the dangling bond and the floating bond\textsuperscript{173,174}.

In the classical MD simulations to generate a-Si, we have run an initial \textit{melting} simulation at 3500 K for 250 ps in the NVE ensemble, with an integration timestep of 0.1 fs using the Verlet leapfrog integration scheme\textsuperscript{153}. After this melting, we quench to 300 K at three rates: \(1 \times 10^{12}\) K/s, \(1.33 \times 10^{12}\) K/s and \(2 \times 10^{12}\) K/s close to literature values\textsuperscript{23}. Thereafter, the structure is further annealed for 100 ps at 600 K. Finally we relax the annealed structure using DFT, as described below, which gives us model structures of pure a-Si. By incorporating hydrogen in the a-Si model to passivate all undercoordinated Si, we have generated three models of a-Si:H, with optimum hydrogen concentrations of 14\%, 15.5\% and 16.5\%. These saturated model structures of a-Si:H are relaxed with GGA-DFT. We also relax two further structures taken from the saturated a-Si:H structures, as example of unsaturated structures with smaller hydrogen concentrations of 12\% and 14.5\%, which are termed “unsaturated” models of a-Si:H. For chapter 4 and 5 the unsaturated and the oversaturated hydrogenated amorphous
silicon are generated by removing and adding hydrogen into or from 14 % hydrogen saturated a-Si structures followed by DFT relaxation.

All structural, electronic and optical properties of a-Si:H were calculated from first-principles after performing ionic relaxations on the classically generated structural models within density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP). The generalized gradient approximation (PW91) to the exchange-correlation functional was applied. The interactions between ion cores and valence electrons are described using the projector-augmented wave method (PAW), with 4 electrons on Si and 1 electron on H. The electronic wavefunctions are described within a plane wave basis set and the kinetic-energy cutoff is set to 400 eV. Irreducible Brillouin zone integration for the supercell of 512-atoms was conducted using Γ point sampling. A Gaussian smearing of width 0.05 eV is applied to determine the band occupations and the width of the electronic density of states peaks.

A concern for these calculations is the severe underestimation of the band gap with GGA-DFT, which we calculate to be 0.7 eV for c-Si, compared to 1.1 eV in experiment. In order to address this fundamental point, further hybrid DFT calculations, using the HSE06 functional, with 25% exact exchange and a screening length of 0.2 Å, are performed at the GGA-DFT geometry to determine more accurately the mobility gaps in our models of a-Si:H.

For GeNW All calculations were performed in a three dimensional periodic supercell model of the nanowires, using a plane wave basis set to describe the valence electron wavefunctions within the VASP.5.2 code. The Perdew Burke Ernzerhof (PBE) GGA approximation to the exchange correlation functional was applied. To test the performance of this GGA-DFT functional, we also carried out hybrid DFT calculations for the smallest diameter modified nanowires using the screened exchange HSE06 functional, with 25% exact exchange and a
screening length of 0.2 Å⁻¹, at the PBE geometry, to determine more accurately the band gap of the Ge nanowires. A plane wave cutoff energy of 400 eV is used and the core-valence interaction is described by the projector augmented wave (PAW) method, with a [Kr] core for Ge and a [He] core for O and N, while a 1 electron H potential is applied. The calculations are performed with cell dimensions normal to the wire axis chosen large enough to reduce interactions between neighbouring wires and induce quasi-1-dimensional periodicity along the wire axis. A full relaxation of the ionic positions with no symmetry constraints has been performed on all nanowire structures with the forces on each atom converged to less than 0.01 eV/Å. k-point sampling is performed with a (1 x 1 x 4) Monkhorst-Pack sampling grid. A Gaussian smearing of width 0.1 eV is applied to determine the band occupations and electronic density of states within the Methfessel-Paxton scheme.

3.6 Preparation of amorphous silicon

Experimentally, there exist several preparation methods for a-Si:H films. Early work on evaporated and sputtered a-Si:H lead to poor quality films, and it is now widely accepted that Radio Frequency (RF) Glow Discharge produces the best quality material, although other more recent CVD methods claim similar or better results. A comprehensive review of the advantages and disadvantages of the different methods employed to grow a-Si:H can be found in the books edited by Searle and Street.

In general, it is desirable that a hydrogen plasma be employed to help the formation of Si-Hn ion radicals; hence, methods based on plasma-enhanced chemical vapour deposition (PECVD) techniques are usually preferred. The ions produced in the plasma region are directed via an electric field towards a substrate, where film growth takes place. A common characteristic of these PECVD techniques is the possibility of tuning the system using several parameters, which might be mutually dependent on or independent of each other, like
partial gas pressure, electrode bias, substrate bias, flow rates, gas mixtures, substrate temperature, and any other adjustable parameter. A review of plasma deposition of a-Si:H can be found in Bruno et al.\textsuperscript{186}.

Computationally, there are several methods of preparation of a-Si:H\textsuperscript{170,187,171,188,189}. One of the first models of a-Si:H was created by Allan \textit{et al.} using the cluster Bethe-lattice approach\textsuperscript{187}. Another class of methods is WWW algorithm\textsuperscript{170}. An improved version of the algorithm is known to generate high-quality models with a modest computation effort. The drawback of this method is that all atoms in the model have exclusively 4-fold coordinated Si and no coordination defects. In 1985 Car and Parrinello simulated the cooling of liquid silicon to obtain a structure of the amorphous phase\textsuperscript{171}. The calculations were performed at the level of density functional theory. This method only works for small systems because of the high computational time demand. Others are based on a slightly different approach. E.g., Klein \textit{et al.}\textsuperscript{188} prepared a sample of a-Si:H using a tight-binding molecular dynamics simulation, by quenching a mixture of silicon and hydrogen from the gas phase at zero pressure.

In our preparation method to produce real coordination defects sample and to study the big system we used the heat and quench method, with classical molecular dynamics implemented in the GULP code. In a heat and quench preparation, one starts from crystalline silicon which is heated to some temperature that should be sufficiently above the melting point so that a liquid is formed, i.e. a disordered structure is present. The melt is then quenched to 300 K fast enough that full crystallization is prevented and the structure is trapped in a non-crystalline arrangement.

We have run the initial melting simulation in GULP at temperatures high enough to cause melting. It is possible that melting could take place at lower temperatures (indeed, the
predicted melting temperature for bulk Si using the Tersoff potential is around 2400 K), however, simulating the process of melting, would require longer simulation times than is practical. Thus, running the melting simulation at high temperature accelerates the process. We have found that the temperature required to form the melt depends on the number of atoms and the dimensionality of the structure in the simulation supercell see table 3.2.

3.2 Table the dependence of number of atoms with Melting Temperature.

<table>
<thead>
<tr>
<th>Structures</th>
<th>Number of atoms</th>
<th>Melting Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk a-Si</td>
<td>512</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>1024</td>
<td>3200</td>
</tr>
<tr>
<td></td>
<td>4098</td>
<td>3000</td>
</tr>
<tr>
<td>a-Si/c-Si interfaces</td>
<td>512</td>
<td>3200</td>
</tr>
<tr>
<td>a-Si/c-Si core-shell nanowires</td>
<td>960</td>
<td>3000</td>
</tr>
</tbody>
</table>

After bulk silicon is melted for 250 ps at 3500 K by the constant volume and energy method (NVE), the resulting liquid is subsequently quenched to 300 K at the following rates: $4 \times 10^{14}$ K/s, $2 \times 10^{14}$ K/s, $1.33 \times 10^{14}$ K/s and $1 \times 10^{14}$ K/s. While the cooling rate employed here is significantly higher than that in the MQ experiments (Calculation: $10^{12}$ K/s, Experiment: $10^6$ K/s), this rate is similar to that realized in laser annealing process and is a tractable quench rate for these simulations. After cooling, the disordered silicon is annealed for 100 ps at 600 K. Finally we relax to 0 K the annealed structure using density-functional theory (DFT), as implemented in the VASP. Figure 3.3 shows the flow chart of preparation of amorphous silicon and hydrogenated amorphous silicon.
Quench rate is one of the crucial parameters in preparing amorphous silicon. It has a defining role in preparing high quality (less defective) amorphous silicon; table 3.3 presents the defect concentration related to the quench rates. We examined different quenching rates in a 512 atoms supercell of a-Si. Table 3.3 shows the average coordination number of a-Si at different quench rates. We found that with the slowest quench rate there was an increase in 4-fold coordinated Si and the computed coordination number shifts towards 4. Thus, a fast quench resulted in the formation of a significant number of under coordinated Si in the bulk. Figure 3.4 shows the coord number distribution for our fastest ($4 \times 10^{14}$ K/s) and our slowest ($1 \times 10^{12}$ K/s) quench rates. At slow quench rate, various coordination numbers composed of primarily...

Fig 3.3 Flow chart of preparation of amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H). Where $T_m =$ melting Temperature, $\tau_m =$ Melting Time, QR = quench rate, $T_a =$ Anneal Temperature, $\tau_a =$ Anneal Time, and R = DFT Relaxation.
threefold, fourfold and fivefold coordination exist. The fourfold coordination predominates, and the fivefold coordination reduces when the quench rate goes down to $10^{12}$ K/s.

Table: 3.3 Average coordination number of Si for different quench rates for 512 atom bulks amorphous Si supercell.

<table>
<thead>
<tr>
<th>Quenched rate K/s</th>
<th>3-fold Coordination (%)</th>
<th>4-fold Coordination (%)</th>
<th>5-fold coordinated (%)</th>
<th>Average coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 10^{14}$</td>
<td>26</td>
<td>51</td>
<td>23</td>
<td>3.75</td>
</tr>
<tr>
<td>$2 \times 10^{12}$</td>
<td>18</td>
<td>75</td>
<td>12</td>
<td>3.86</td>
</tr>
<tr>
<td>$1.33 \times 10^{12}$</td>
<td>15</td>
<td>78</td>
<td>12</td>
<td>3.87</td>
</tr>
<tr>
<td>$1 \times 10^{12}$</td>
<td>12</td>
<td>83</td>
<td>5</td>
<td>3.90</td>
</tr>
</tbody>
</table>

Figure 3.4 Distribution of coordination of number of a-Si (a) fast quenching rate ($4 \times 10^{14}$ K/s), (b) slow quenching rate ($1 \times 10^{12}$ K/s).
We also show in figure 3.5 the silicon-silicon radial distribution function (RDF) from the different quench rates. We observe that slower cooling rate ($1 \times 10^{12}$ K/s) results of amorphous silicon shows defined peaks with higher values of the first and second maximum of the radial distribution function $g(r)$. The lowest quench rate sample gives very good agreement with experiment.$^{67, 166}$

**Fig. 3.5**: Quench rate dependent RDF for 512 atom bulk Si (a) Melting Temperature (b) quench rate $4 \times 10^{14}$ K/s (c) quench rate $2 \times 10^{12}$ K/s (c) quench rate $1.3 \times 10^{12}$ K/s (d) quench rate $1 \times 10^{12}$ K/s (f) Crystalline.

For each quench rate, the five samples of a-Si:H all produce similar structural data. As a check on the effect of supercell size, supercells with 1024 atoms of bulk a-Si is produced from the heat and quench approach, and comparison of the structural properties between the 512 atom bulk a-Si supercell shown in figure 3.6 and these supercells showed no significant
effects due to supercell size, so that we consider the 512 atom bulk a-Si supercell sufficiently converged.

![Graph showing radial distribution function](image)

**Figure 3.6** Calculated radial distribution function of 1024 atom bulk amorphous silicon

The quench rate has also great impact of producing high quality electronic structure for example Figure 3.7 shows a DOS plot for a-Si with 512 atoms from different quench rates VASP relaxation. As we can see from figure 3.7 there are states round the Fermi level but these states decrease with slower quench rates i.e. this is because the number of formed of dangling bonds in a-Si decreases at slow quench rates.
Figure 3.7 Total density of states of 512 atom bulk a-Si at different quench rates after VASP relaxation. The Fermi level is shifted to 0.
CHAPTER 4

4 The Dependence of the Optical and Mobility Gaps of Hydrogenated Amorphous Silicon on Hydrogen Concentration

4.1 Introduction

In this chapter we study the dependency of the optical and mobility gaps of hydrogenated amorphous silicon on the H content up to hydrogen saturation. The optical absorption properties of hydrogenated amorphous silicon (a-Si:H) are important in solar applications and from the perspective of fundamental materials science. However, there has been a long standing question from experiment of the dependence of the optical gap on the hydrogen content in a-Si:H. To reconcile this debate, we present density functional theory simulations of models of hydrogenated a-Si:H, with different hydrogen concentrations, up to and including full hydrogen saturation. We discuss the dependence of the optical and mobility gaps in fully saturated and undersaturated a-Si:H. Oversaturation of a-Si:H will be discussed in chapter 5. For undersaturated hydrogen contents, both gaps increase with increasing hydrogen concentration until hydrogen saturation is achieved. Our key finding is that, at saturation, the optical and mobility gaps converge to a value independent of the hydrogen content. Our analysis thus resolves the contradiction between experimental data examining the effect of hydrogen content up to saturation and interpretations based on conventional expectations regarding the hydrogen dependence of the optical and mobility gaps up to saturation, and provides new insight on the materials properties of hydrogenated amorphous silicon that can be used for sample preparation.
In this chapter we generate a-Si, run a “melting” simulation of a 512 atom Si supercell (a (4 x 4 x 4) supercell expansion) at 3500 K for 250 ps in the NVE ensemble, with an integration timestep of 0.1 fs and Verlet leapfrog integration. We quench to 300 K at three rates: \(1 \times 10^{12}\) K/s, \(1.33 \times 10^{12}\) K/s and \(2 \times 10^{12}\) K/s to give three a-Si structures with different defect concentrations, which is necessary for analysing the effect of local atomic structure in a-Si:H on the optical and mobility gaps. This procedure is repeated in 5 heat and quench simulations for each quench rate, giving an ensemble of a-Si structures that have the same saturation H content for each quench rate. The structure is annealed for 100 ps at 600 K and we relax using DFT to obtain pure a-Si from different H contents. By incorporating hydrogen into the a-Si model to passivate all undercoordinated Si, we generate three models of a-Si:H, with saturation hydrogen concentrations of 14 %, 15.5 % and 16.5 % (relaxed with DFT as described below) for the slowest to fastest quench rates. Undersaturated structures a-Si:H with H concentrations of 12 % and 14.5 %, were generated by reducing the H content by 2 % from the corresponding saturated structure.

A concern in these calculations is the severe underestimation of the band gap with GGA-DFT, which we calculate as 0.7 eV for c-Si, compared to 1.1 eV in experiment. In order to address this, further hybrid DFT calculations, using the HSE06 functional, with 25 % exact exchange and a 0.2 Å\(^{-1}\) screening length, are performed at the GGA-DFT geometry to determine more accurately the mobility gap of a-Si:H.

### 4.2 The Optical Gap of Hydrogenated Amorphous Silicon

The optical band gap, \(E_{\text{opt}}\), of a-Si and a-Si:H and its dependence on hydrogen concentration are obtained by extrapolating the linear part of the function \([\alpha(E) \times E]^{1/2}\) plotted against photon energy, \(E\), giving a standard Tauc plot.
Figure 4.1 Linear extrapolation to determine the optical band gap (Tauc plot) for an optimum hydrogen concentration of a-Si:H with (a) 14.0 % H (b) 16.5 % H, (e) 15.5 % H for an unsaturated hydrogen concentration of a-Si:H with (c) 12.0 % H and (d) 14.0 % H.

Figure 4.1 (a-b) and 1 (e) show a typical Tauc plot for determining the optical gap of a-Si:H with saturation hydrogen concentrations of 14 %, 15.5 % and 16.5 % (quench rates of $1\times10^{12}$ K/s, $1.33\times10^{12}$ K/s and $2\times10^{12}$ K/s). Our calculated imaginary dielectric function and
absorption coefficient versus energy plot shown in figure 4.2 are consistent with experimental results, e.g. references \(^{31}\) and \(^{77}\), showing in particular the correct Urbach behaviour (the exponential increase in absorption coefficient with photon energy at sub-gap energies), which, together with structural analysis presented below, gives good confidence in our models of a-Si:H.

![Graph showing imaginary part of dielectric function and absorption coefficient versus energy](image)

**Figure 4.2:** (a) Computed imaginary part of the dielectric function for c-Si a-Si:H with 14\%, 15.5\% and 16.5\% H contents. (b) Plot of the optical absorption coefficient, \(\alpha\), as a function of photon energy of a-Si:H from DFT calculation with the H content indicated in the figure.

We extract an optical gap of 1.25 eV for all a-Si:H structures with optimum hydrogen concentrations, that is, 14\%, 15.5\% and 16.5\% for each quench rate. To our knowledge, optical gaps for a-Si:H have not been studied with DFT, which has tended to focus on the nature of the band tails and the mid-gap defect states resulting from the amorphous structure.
and undercoordinated Si. The energy gaps shown in table 4.1 include comparison with available experimental data. These results show that the optical gap of a-Si:H does not depend on the H concentration at full hydrogen saturation and this is a key contribution from theory to the experimental debate regarding the secondary role of hydrogen content in determining the optical band gap of a-Si:H\textsuperscript{77}, in which experimental data show that for certain moderate hydrogen concentrations there is no change in optical gap\textsuperscript{73,190, 75} although this is not always the interpretation. We see that although we have generated three different a-Si:H model structures, with particular atomic structures and defect densities, fully saturating with hydrogen results in the same optical gap.

![Figure 4.3: Linear extrapolation to determine the optical band gap (Tauc plot) for different quench rate of a-Si (a) 1.0 \times 10^{12} \text{ K/s} (b) 1.33 \times 10^{12} \text{ K/s} and (c) 2.0 \times 10^{12} \text{ K/s}.](image-url)
There remains the question of the origin of the undeniable decrease of $E_{\text{opt}}$ by lowering the H concentration that is found experimentally.\textsuperscript{71,72,76} To investigate the effect of H concentration on $E_{\text{opt}}$, we calculate the optical band gap for undersaturated H contents, by reducing the hydrogen concentration in 14 % and 16.5 % saturated a-Si:H by 2 % and 2.5 %.

The Tauc plots for 12 % and 14 % unsaturated a-Si:H are shown figure 4.1 (c) and (d), with the optical gaps given in table 4.1. When compared to samples having optimum hydrogen contents, the optical gap is reduced and a reduction in H concentration of 2 % is enough to significantly change $E_{\text{opt}}$ (~0.1 eV). Furthermore, structures that are even less saturated show smaller optical gaps (see figure 5.7 (a-d) in the chapter 5). In particular, unhydrogenated a-Si samples generated from $1 \times 10^{12}$ K/s, $1.33 \times 10^{12}$ K/s, and $2 \times 10^{12}$ K/s quench rates yield optical gaps of 0.92 eV, 1 eV and 1.08 eV, respectively (see figure 4.3). The different gaps result from different defect densities from each quench rate.
Figure 4.4 DFT relaxed atomic structure of (a) 512 atom bulk a-Si model (b) bulk a-Si:H with 14 % H, (c) bulk a-Si:H with 15.5 % H and (d) bulk a-Si:H with 16.5 % H saturation content.

Table 4.1 Optical ($E_{opt}$) and mobility ($E_{mob}$) gaps for different hydrogen concentrations in a-Si:H. Also included are experimental results from refs. 13 and 14.

<table>
<thead>
<tr>
<th>H concentration in a-Si:H</th>
<th>$E_{opt}$ (eV)</th>
<th>$E_{mob}$ (eV)</th>
<th>$E_{mob}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GGA-DFT</td>
<td>Hybrid DFT</td>
</tr>
<tr>
<td>14 % saturated</td>
<td>1.25</td>
<td>1.27</td>
<td>1.83</td>
</tr>
<tr>
<td>12 % unsaturated</td>
<td>1.16</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>16.5 % saturated</td>
<td>1.25</td>
<td>1.29</td>
<td>1.85</td>
</tr>
<tr>
<td>14 % unsaturated</td>
<td>1.17</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>15.5 % saturated</td>
<td>1.25</td>
<td>1.28</td>
<td>1.84</td>
</tr>
<tr>
<td>Experimental Results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{\text{opt}}$ (eV)</td>
<td>$E_{\text{mob}}$ (eV)</td>
<td></td>
</tr>
<tr>
<td>Cody et al., ref. [77]</td>
<td>1.70 ±0.03</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Lee et al., ref. [13]</td>
<td>1.73 - 1.76</td>
<td>1.88 - 1.90</td>
<td></td>
</tr>
</tbody>
</table>

Our results indicate two regimes of hydrogen concentration – one is the low hydrogen concentration regime, in which a-Si:H is not saturated and the H concentration determines $E_{\text{opt}}$. The other regime is where a-Si:H is saturated and the H concentration has no effect on the optical gap, regardless of the actual H concentration. This is consistent with Cody’s finding for samples with two varying, but saturated, H concentrations but the same optical band gap.

### 4.3 Structural Properties of Hydrogenated Amorphous Silicon

We now examine the atomic structure of our models of a-Si and a-Si:H, figure 4.4 shows the atomic structure of a-Si and a-Si:H (with 14%, 15.5% and 16.5% hydrogen saturation concentration) after the GGA-DFT relaxation. Figure 4.5 (a) – (d) shows the radial distribution function (RDF) plots, figure 4.6 (a) – (d) shows the vibrational density of states (VDOS) for saturated (14% and 16.5% H content) and unsaturated (12% and 14% H content) a-Si:H and figure 4.7 (a-d) shows the Si angle distribution (corresponding to the tetrahedral angle in crystalline silicon).
Figure 4.5 Plots of radial distribution function for a-Si and a-Si:H. (a) quench rate of $1.0 \times 10^{12}$ K/s and a 14.0 % hydrogen concentration in a-Si:H (b) a quench rate of $2 \times 10^{12}$ K/s and a 16.5 % hydrogen concentration in a-Si:H (c) same quench rate as part (a), but with 12.0 % H content and (d) same quench rate as part (b), but with 14.0 % H content.

For a-Si:H with 14 % H, Si-H bonds dominate (~95 %) and the remainder are Si-H$_2$ (4 %) and Si-H$_3$ bonds (1 %); the other saturated a-Si:H structures show only small differences in the distributions of SiH$_n$ species, e.g. for 16 % H, 5 % of Si-H are silicon dihydrates. Such bonds have been observed in experiment using infrared spectroscopy$^{191}$. The average coordination number is 3.92 (14 % H) compared to 3.88 from experiment$^{166}$. 

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First Principles Modeling of Hydrogenated Amorphous silicon
The Si-Si RDF plots for a-Si:H show better defined peaks with higher values of the first and second maximum of the RDF when compared with a-Si, but still show amorphous character. These structural data are in very good agreement with experiment and previous calculations\textsuperscript{78,79,80,166,67,23}, in particular for a-Si:H generated in references\textsuperscript{78-80}. The modification to the RDF results from hydrogen reducing the number of undercoordinated Si atoms. Hydrogen not only passivates dangling bonds but at the same time decreases the highly strained bonds which are present in amorphous silicon\textsuperscript{69}. Generally when we look at our structure the majority of short Si-Si bonds (bonds with shorter Si-Si bond lengths than equilibrium) are contributed by silicon atoms saturated by hydrogen. These results are consistent with, e.g. reference\textsuperscript{171}.

![Figure 4.6: Computed vibrational density of states for (a) 14 % and 16.5 % of saturated a-Si:H (c) and (d) 12 % and 14 % unsaturated a-Si:H. See figure 4.5 caption for more details.](image)
We further characterise the structure of a-Si:H in both the hydrogen saturation and undersaturation regimes by the vibrational density of states in figure 4.7 and the Si angle distribution in figure 4.7. These are entirely consistent with previous experimental results\textsuperscript{31,192,193,194} and calculations on a-Si:H\textsuperscript{195,23,193-194}. We note that the spread in the Si angle distribution and the two prominent peaks in the VDOS are well reproduced in this work compared to references\textsuperscript{196,196,23,192-193}. This comparison of the structural data from our a-Si and a-Si:H models with previous work gives confidence in using these a-Si:H models to analyse the optical and mobility gaps and effects due to H content, even though these structures have been generated from heat and quench simulations.

Figure 4.7: Si angle distribution for (a) 14 % and 16.5 % of saturated a-Si:H (c) and (d) 12 % and 14 % unsaturated a-Si:H. See figure 4.5 caption for more details.
4.4 Mobility Gap of Hydrogenated Amorphous Silicon

To investigate how the electronic properties and mobility gaps evolve with composition in a-Si:H, we investigate the nature of wavefunctions and their respective contributions to the density of states (DOS).

Figure 4.8 shows the IPR for saturated and unsaturated a-Si:H structures around the Fermi level (referenced to 0 eV). We limit our presentation to eigenstates which are mid-gap and near the mobility edges. In our a-Si:H models, a value for the IPR larger than ~9 corresponds to a localized electronic state, otherwise the electronic state is extended. We then determine the positions of the valance band mobility and conduction band mobility edges from the localised to delocalisation transition.
Figure 4.8: Plots of semi-log density of states (red line) and Inverse Participation Ratio (IPR, green histogram) versus energy in a-Si:H, with (a) 14 % H content, (b) 12 % H content (undersaturated from (a)), (c) 16.5 % H content and (d) 14 % H concentration (undersaturated from (c)) (e) 15.5 % H content.

Mid-gap states have a large IPR, consistent with their localised nature. From the IPR of fully saturated a-Si:H models, we obtain invariant mobility gaps of 1.27 eV, 1.28 eV and 1.29 eV for a-Si:H with 14 %, 15.5 % and 16.5 % H content, respectively. Similar to the optical gap, we find that irrespective of the precise local atomic structure in the a-Si:H model, full saturation with hydrogen always gives the same mobility gap. Dong and Drabold estimated a mobility gap of 1.20 eV in a model a-Si structure using a tight binding Hamiltonian \(^{197}\).
Figure 4.9 Plots of semi-log density of states (red line) and Inverse Participation Ratio (IPR, histogram) versus energy from hybrid DFT (HSE06) (a) 14% hydrogen concentration in a-Si:H (quench rate =1 x10^{12} K/s, (b) 15.5% hydrogen concentration (quench rate =1.33 x10^{12} K/s) and (c) 16.5% hydrogen concentration (quench rate =2 x10^{12} K/s).

Given the underestimation of the energy gap with GGA-DFT, we further calculated $E_{mob}$ using hybrid DFT (HSE06, figure 4.9), which gives mobility gaps in better agreement with experiment, being 1.83 eV, 1.84 eV and 1.85 eV for the fully saturated a-Si:H models, which compare well with the experimental value of 1.88 – 1.90 eV^{13,15}. Considering the
fundamental GGA-DFT and confidence errors, our results indicate that, similar to the optical gap, the a-Si:H mobility gap is independent of hydrogen content for samples with optimum hydrogen concentration.

For the undersaturated models with 12 % and 14 % H concentration and undercoordinated Si defects, the mobility gap is reduced (table 1). In all cases the mobility gap is larger than the optical gap, which is well known from experiment\textsuperscript{13, 15} giving further confidence in the present results.

Finally, while the IPR in figure 4.8 demonstrates the localized-to-extended transition occurring near the valence and conduction bands, the combined plots of the IPR and the density of states indicate the role of hydrogen in suppressing the mid-gap defect states originating from undercoordinated Si atoms. For the fully saturated structures there are band tails with localised states but no states around the Fermi level. Reducing the hydrogen content to below optimum concentration results in the appearance of mid-gap states with high IPR. Charge density analysis confirms that these correspond to Si with dangling bonds. The differences in the IPRs between localized states near the conduction and valence mobility edges arise from their nature: the conduction band is composed from empty spherically symmetrical Si s-like states not influenced by bond angle disorder. In contrast, the valence band is composed of Si p-like states, strongly affected by bond angle distortions.

### 4.5 Conclusions

GGA-DFT and hybrid DFT calculations on large structural models of amorphous silicon, allow us to examine for the first time from first-principles the effect of H concentration, up to saturation H content, on the optical and mobility gaps in a-Si:H. Given the complexity in the structure of a-Si:H with hydrogen oversaturation, we consider this regime of H saturation
concentration in chapter 5. Our major finding is that the optical and mobility gaps of a-Si:H do not depend on H concentration once saturation of undercoordinated silicon atoms is achieved and those changes in both energy gaps as a function of H-content arise from undersaturation in the H concentration.

Comparing these findings with experiment, we resolve for the first time the ambiguity that exists regarding the effect of H-content on the optical and mobility gaps of a-Si:H. Cody’s original work\textsuperscript{77} is unambiguous regarding the optical gap with H concentration. However, subsequent work generally concludes that the optical gap of a-Si:H depends on hydrogen concentration. While some of these conclusions are correct for undersaturated H contents\textsuperscript{73, 75, 190}, a mis-interpretation of the dependence of the optical gap on hydrogenation is apparent. Data for the optical gap as a function H concentration are clear that once the hydrogen concentration exceeds around 9 \%, the optical gap of a-Si:H is independent of the hydrogen concentration\textsuperscript{73, 75, 190}. In contrast, for smaller hydrogen concentrations, the dependence on H-content is clear. However, the interpretation from the literature is still that H concentration affects $E_{\text{opt}}$. Our results show that the optical and mobility gaps of a-Si:H, are unchanged at saturation H content and indicate an incorrect interpretation of experimental data. In light of this reinterpretation, the accepted view that the optical and mobility gaps of a-Si:H depend on H concentration, at least up to H saturation, needs to be modified to accommodate the effects of hydrogen saturation. Notwithstanding the dynamics of hydrogen in devices, finding optimum preparation conditions, such as H\textsubscript{2} concentration or substrate temperature, can ensure fabrication of a-Si:H where disorder rather than hydrogen concentration is the major determinant of material properties.
CHAPTER 5

5 Analysis of the Effect of Hydrogen Concentration in Hydrogenated Amorphous Silicon on the Formation of Strained Si-Si Bonds and the Optical and Mobility Gaps

5.1 Introduction

In this chapter we study in detail how the atomic geometry is influenced by hydrogen undersaturation and mild hydrogen oversaturation and how this determines the optical and mobility gaps. The optical and mobility gaps show a volcano curve as the hydrogen content varies from undersaturation to mild oversaturation, with largest gaps obtained at the saturation hydrogen concentration. At the same time, mid-gap states associated with dangling bonds and strained Si-Si bonds disappear at saturation but reappear at mild oversaturation which is consistent with the evolution of optical gap. The distribution of Si-Si bond distances provides the key to the change in electronic properties. In the undersaturation regime the new electronic states in the gap arise from the presence of dangling bonds and strained Si-Si bonds, which are longer than the equilibrium Si-Si distance. Increasing hydrogen concentration up to saturation reduces the strained bonds and removes dangling bonds. In the case of mild oversaturation the mid-gap states arise exclusively from an increase in the density of strained Si-Si bonds. Analysis of our structure shows that the extra hydrogen atoms form a bridge between neighbouring silicon atoms, thus increasing the Si-Si distance and increasing disorder in the sample, which impacts on the optical and mobility gaps.

Many studies of a-Si:H examine the impact of H concentration from undersaturation to saturation. In this chapter we focus on the impact on a-Si:H optical and mobility gaps resulting from a small increase (< 4 %) in the concentration of hydrogen beyond saturation,
which we term mild oversaturation, and for which we have not found any previous studies in the literature. This regime of H content is distinct from that studied in references\textsuperscript{78-80}, in which hypersaturation of H is used to generate nanoscopic regions of c-Si in an a-Si:H matrix through a continuous flux of hydrogen. A 4% increase in H content past saturation is chosen as it does not lead to formation of c-Si domains, permits the regime of mild oversaturation to be explored and allows us to still have a reasonable computational expense in a 512 Si atom supercell.

Our a-Si structure is generated by the procedure described in chapter 3. Incorporating H into the heat and quench generated a-Si (section 3.6) passivates the dangling Si formed during preparation. We consider in detail a model system based on 14% H that saturates a-Si from a 1x 10\textsuperscript{12} K/s quench rate. To examine how the H content, at both under- and mild oversaturated regimes, affects the atomic structure and optical and mobility gaps, we generate further six a-Si:H structures. Four of them are undersaturated and obtained by removing H from the 14% saturated structure with H concentrations of 7%, 9%, 12%, and 13%. The remaining two a-Si:H structures are mildly oversaturated, by adding H to the 14% saturated structure, with H concentrations of 16% and 18% H. Each undersaturated and mildly oversaturated a-Si:H is fully relaxed with DFT.

### 5.2 Structural analysis of hydrogenated amorphous silicon with different H concentrations

The structural analysis of a-Si:H allows us to examine both the quality of the amorphous structure generated from the heat and quench procedure and any effects arising from H content. For this analysis we obtained the radial distribution function (RDF), the vibrational density of states, the tetrahedral angle distribution and the distribution of Si-Si bond lengths.

In Figure 5.1 (a-c) we show a typical atomic structure for a-Si:H (with undersaturated, 7%,
saturated, 14%, and mildly oversaturated, 18%, H concentrations) relaxed with GGA. In H-saturated a-Si:H structure, H is predominantly present in Si-H bonds, comprising 95% of all Si-H\textsubscript{n} bonds, and the remainder is bonded forming Si-H\textsubscript{2} (4%) and Si-H\textsubscript{3} (1%). Si-H\textsubscript{n} bonds have been observed experimentally from infrared spectroscopy\textsuperscript{191}. The formation of lower number of Si-H\textsubscript{2} bonds is good indication good grade hydrogenated amorphous silicon\textsuperscript{198}.

Figure 5.1 Structural models for 512 Si atom with (a) 14% H concentration in saturated a-Si:H, (b) 7% H concentration in undersaturated a-Si:H and (c) 18% H concentration in mildly over saturated a-Si:H. Si are yellow spheres and H are white spheres.
The average coordination numbers in a-Si:H with 7%, 14% and 18% H concentrations are 3.80, 3.92 and 4.01, respectively. Our value for saturated a-Si:H compares well with the experimental value of 3.88 for H-saturated a-Si:H\textsuperscript{55}, while the value for mild oversaturation indicates a higher concentration of 5-fold coordinated Si atoms, there being 8 such Si atoms.

We show the Si-Si RDF as a function of H concentration in Figure 5.2. In general, the RDF is typical of a-Si and a-Si:H, with a well-defined peak at the nearest neighbour Si-Si distance and broadened and flattened peaks for the remaining Si-Si distances that are characteristic of the lack of long range order in a-Si and a-Si:H. The obtained RDF is also consistent with previous theoretical and experimental work\textsuperscript{78-80, 166, 199}.

![Figure 5.2 Si-Si radial distribution functions in a-Si and a-Si:H for different % H contents.](image)

The VDOS of a-Si and for a-Si:H different H concentrations are plotted in Figure 5.3. For all calculations we have found no negative frequencies, which shows that our systems are in a...
local minimum. As we can see from Figure 5.3, the position of transverse acoustic (TA) mode, centred at 20 meV, and transverse optical (TO) mode, centred at 62 meV, are in reasonable agreement with the positions of the experimental TA and TO peaks, at 20 and 61 meV\textsuperscript{192-193}.

![Figure 5.3](image_url)  

**Figure 5.3** Vibrational density of states for bulk a-Si and a-Si:H with different H contents.

Figure 5.4 shows the distribution of Si-Si-Si tetrahedral angles for a-Si and a-Si:H with different H concentrations. The overall shape of the angle distribution is consistent with earlier works\textsuperscript{23, 67}, again confirming that our models are reasonable. The peak around the crystalline Si tetrahedral angle of 109.5° generally narrows as H is added to the system.
5.2.1 **Optical properties of hydrogenated amorphous silicon**

The experimental optical gap of device quality $a$-Si:H is in the range between 1.70 to 1.80 eV\textsuperscript{13, 15} and the impact of H content on the in $a$-Si:H around H saturation has been already discussed in reference\textsuperscript{63} and chapter 4. Considering $a$-Si:H at undersaturation, our Tauc plots give $E_{\text{opt}} = 1.04, 1.09, 1.16$ and 1.20 eV, as shown in Figure 5.5 for H contents of 7, 9, 12 and 13\% respectively, and $E_{\text{opt}} = 0.92$ eV for non-hydrogenated $a$-Si. As discussed in the chapter 4 the size of the change in the optical gap with H content is significant and is consistent with experimentally determined band gap changes\textsuperscript{73, 75-77, 190}. Although GGA-DFT clearly underestimates the band gap of Si, the behaviour of our computed optical band gap as function of H content is in reasonable agreement with the experimental results\textsuperscript{63, 73, 75-77, 190}.

![Figure 5.4 Tetrahedral angle distribution for bulk a-Si and a-Si:H with different H content.](image)
We are presently unable to perform hybrid DFT calculations of the optical gap of these structures, but show in figure 5.9 and in reference 63 some hybrid DFT results for the mobility gap, which gives extra confidence in the GGA-DFT results. When we consider higher H concentrations, for which the Tauc plots are shown in Figure 5.6, the extracted optical gaps are 1.25, 1.22 and 1.15 eV for 14%, 16% and 18% respectively. Here, we see that mild oversaturation with H in fact leads to a reduction in the optical gap of a-Si:H, as compared to saturated a-Si:H.
Figure 5.6 Tauc plots to obtain the optical band gap of a-Si:H for H saturated (14%) and mildly oversaturated (16%, 18%) a-Si:H.

5.2.2 Mobility Gap and Electronic properties of hydrogenated amorphous silicon

To investigate how the electronic properties in the gap evolve with H content, we have calculated the IPR (see chapter 3) for undersaturated, saturated and mildly oversaturated H contents in a-Si:H. We have determined the individual atomic contributions to the total IPR for a localized eigenstate, to associate that state with particular structural irregularities. This provides a good indication for the various defect structures that emerge in our models. Since
the important electronic states are those near to the Fermi level, our presentation deals only with the energy eigenvalues which are at mid-gap or near the band-tails of the spectrum.

Figure 5.7 Plots of semi-log density of states (red line) and Inverse Participation Ratio (IPR, histogram) for undersaturated (7%, 9%, 12% and 13%) a-Si:H.

Figure 5.7 shows the semi-log plot of density of states and IPR versus energy for undersaturated a-Si:H. The density of electronic states around the Fermi level clearly decreases as the H concentration increases from 7 to 14%, which we will discuss further below. At 14% H concentration (fully saturated a-Si:H) the midgap states are removed, since this structure has neither dangling bonds nor extra H atoms implying midgap states are minimized. In Figure 5.8 we also show the semi-log density of states and IPR for H concentrations of 16% and 18% H in a-Si:H. In the case of mild over saturation we find new states in the gap, which
similar to H-undersaturation is consistent with the change in the optical gap with H oversaturation and will also be discussed below.

Figure 5.8 Plots of semi-log density of states (red line) and Inverse Participation Ratio (IPR, histogram) for saturated (14%) and over saturated (16%, 18%) a-Si:H.

We see that the IPR evolves with H content. For a-Si:H there are localized states around the band edges, arising from the well-known structural features present in a-Si:H, and these states appear around the Fermi level for both undersaturation and mild oversaturation. The computed mobility gaps, as the difference in energy between the valence and conduction mobility edges are indicated in Figures 5.7 and 5.8, are 1.03, 1.13, 1.16, 1.24, 1.27, 1.25 and 1.22 eV for 7%, 9%, 12%, 13% 14%, 16% and 18% H concentration, respectively.
Figure 5.9 Plots of semi-log density of states (red line) and Inverse Participation Ratio (IPR, histogram) versus energy from hybrid DFT (HSE06) for (a) undersaturated (7%) (b) saturated (14%) and (c) oversaturated (18%) a-Si:H.

To examine the impact of the band gap underestimation with GGA-DFT, we plot in Figure 5.9 the IPR from hybrid DFT for one H concentration in each regime of hydrogen content. The mobility gaps of a-Si:H with 7%, 14% and 18 % H concentrations are computed as 1.62, 1.83 and 1.76 eV. The hybrid DFT mobility gap has already been shown to be in very good agreement with experiment in chapter 4 and the behavior of the mobility gap versus H content is consistent with the behavior obtained from the GGA-DFT calculations, giving confidence to our conclusions from GGA-DFT results.
The mobility and optical band gaps are plotted against the H concentration in a-Si:H in Figure 10. Both have their maximum value for the saturated H concentration. The relationship between the optical and mobility gaps and the H content is represented by a volcano-like curve, such that the optical and mobility gaps reach a maximum at H saturation. For the mobility gap, we compared the hybrid DFT mobility gap at one example in each regime of hydrogen concentration (undersaturated, saturated and mildly oversaturated) and comparison with the corresponding GGA-DFT mobility gap shows the consistency of the GGA-DFT findings regarding the behaviour of the mobility gap with hydrogen content. To the best of our knowledge, this result showing directly the evolution of the optical and mobility gaps in a-Si:H from H undersaturation to mild oversaturation has not been presented before.

![Graph](image)

Figure 5.10 Mobility and optical band gap energies as a function of H concentration in a-Si:H. The green squares are the hybrid DFT values of the mobility gap.

To understand the behavior of optical and mobility gaps in a-Si:H as function of H concentration, in particular with mild H oversaturation, we examine in detail the electronic
density of states (EDOS) and the local atomic structure. The total EDOS of a-Si:H is shown in Figure 5.11 for different H contents. Examining the region around the Fermi level (set to 0 eV) we see a zero EDOS in the case of H saturation (14%). Both for under (7%, 9% 12% and 13%) and over (16% and 18%) saturation there is a finite, non-zero EDOS around the Fermi level. The non-zero EDOS in the gap results in a reduction of the optical and mobility gaps and is consistent with the behaviour of the H content. The non-zero EDOS states enhance charge recombination and causes of a degradation of solar cell performance\textsuperscript{50}.

Figure 5.11 Total DOS for a-Si:H with different H contents. (as indicated)The Fermi level is set to 0 eV.
For H undersaturation, the finite EDOS around the Fermi level should arise primarily from the formation of dangling silicon bonds, as well as from elongated strained Si-Si bonds, as is discussed in the literature\textsuperscript{69}. For the oversaturation case the origin of the finite EDOS is not so obvious, since there are no dangling bonds in this system, so we seek another explanation.

![Graph showing Si-Si bond length distribution](image)

**Figure 5.12** Distribution of Si-Si-bond lengths for a-Si and a-Si:H with different H concentrations.

We present a more detailed structural description of mildly oversaturated a-Si:H through analysis of the Si-Si bond length distribution, which is shown in Figure 5.12 for a-Si and a-Si:H with different H concentrations. This distribution is calculated by defining the cut-off distance for an Si-Si bond up to the first minimum in the correlation functions of each sample. This distribution function shows a sharp peak at around 2.34 Å for all H contents,
with a noticeable tail of longer Si-Si bonds. The Si-Si bond distribution of a-Si and a-Si:H with a H content of 18% shows notable deviations from the perfect tetrahedral network and a bond length distribution that extends to Si-Si distances of about 2.70 Å. Dangling bonds have distances to their nearest non-bonded Si neighbor significantly longer than this (3.20 Å).

Focusing now on the variation of the long, or strained, Si-Si bonds with H content, we see that the presence of these bonds decreases as the H content increases up to saturation and the tail for fully saturated a-Si:H is the smallest of all our samples (see inset of Figure 5.12) consistent with a reduction in the density of states of in the mid gap as a result of removing longer Si-Si bonds. As the H content increases beyond saturation, there is a significant re-emergence of long Si-Si bonds, clearly visible in the tail of the distribution. Thus, as the H content increases beyond saturation, strained Si-Si bonds appear again.

To examine the local atomic structure of the strained Si-Si bonds, we show in Figure 5.13 a section of our a-Si:H structure with a H content of 18%. Here, silicon is indicated by yellow spheres, H by white spheres and the green spheres indicate H atoms that bridge neighboring silicon atoms. The bridging H and the two silicon it bridges can be clearly seen in Figure 5.13. The formation of these Si-H-Si bridges generates 5-fold silicon atoms that have elongated Si-Si distances: from 2.40 Å at saturation to 2.64 Å at mild oversaturation. Therefore, this provides an origin for the mid-gap states in over saturated a-Si:H which we expand on below. This bridging H atom in oversaturated a-Si:H was also observed in Maroudas’s and Stuckelberger’s works even though different methods to prepare a-Si:H samples have been used.
Figure 5.13 Atomic structure of a section of the structural model for mildly oversaturated a-Si:H with a H content of (a) 16% and (b) 18%. Si are yellow spheres, H are white spheres and green spheres are also H atoms that make bridges between silicon atoms.

To further confirm the origin of the mid-gap states in oversaturated a-Si:H, the projected density of states of one undersaturated (7%), saturated (14%) and oversaturated (18%) a-Si:H sample are shown in Figure 5.14, for different types of Si-Si bonds. These are Si-Si bonds shorter than equilibrium, Si-Si bonds longer than equilibrium and dangling Si bonds. For 14% and 18% H contents there are no dangling bonds present, so they cannot be the origin of the mid-gap states at mild oversaturation of H.
Figure 5.14 Projected density of states of (a) unsaturated (7%), (b) saturated (14%) and (c) oversaturated (18%) of a-Si:H.

We see that the band edge states of undersaturated 7% a-Si:H have their origin in the dangling Si, but that the mid-gap states have strong contributions from the dangling Si and from strained (long) Si-Si bonds, consistent with the Si-Si bond distribution in Figure 5.13. For hydrogen saturation (14%), the shorter and strained Si-Si bonds are insignificant. For oversaturated a-Si:H, the mid-gap states are derived almost entirely from the strained Si-Si bonds which have arisen as a result of the incorporation of extra H. The short Si-Si bonds make a minor contribution to the mid-gap EDOS. Thus, the importance of strained Si-Si...
bonds in a-Si:H for determining the optical and mobility gaps of a-Si:H is clear. Analysis of our structures shows that, in addition, a fraction of the extra H atoms form a bridge between neighboring silicon atoms and increase the Si-Si distance, promoting bond length disorder in the sample. That has the potential to enhance the Staebler-Wronski effect.

5.2.3 Conclusions

We have used DFT calculations, both GGA-DFT and hybrid DFT, to show that a-Si:H exhibits a maximum in the optical and mobility gaps with H concentration. The optical and mobility gaps show a volcano curve as the H content is varied from 7% (undersaturation) to 18% (mild oversaturation). At the same time, mid-gap states associated with dangling Si and strained Si-Si bonds disappear at saturation but reappear at mild oversaturation, in consistency with the evolution of the optical gap. Standard structural analyses of our models are unable to provide a detailed description of the influence of H content. The distribution of Si-Si bond distances provides the key to the change in electronic properties. In the undersaturation case, the new electronic states in the gap arise from the presence of dangling and strained Si-Si bonds, which are longer than the equilibrium Si-Si distance. Increased H concentration up to saturation reduces the strained bonds and removes dangling bonds. In the case of mildly over saturation the mid-gap states arise exclusively from an increase in the density of strained Si-Si bonds. Analysis of our structures shows that, in addition, a fraction of the extra H atoms form a bridge between neighboring silicon atoms and increase the Si-Si distance and promoting bond length disorder in the sample. That has the potential to enhance the Staebler-Wronski effect.

Please note that Chapters 6-8 (pp.103-198) are unavailable due to a restriction requested by the author.