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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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Finally, a special thanks to my family. Words cannot express how grateful I am to my sisters and brothers for all of the sacrifices that you have made on my behalf. Your prayer for me was what sustained me thus far. I would also like to thank all of my friends specially for Eliase and Daniel incented me to strive towards my goal. At the end I would like express appreciation to my beloved fiance Tizita Desalegn and to my son Bemnet Merid who spent sleepless nights with and was always my support.
# LIST OF ACRONYMS

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<tr>
<th>Acronym</th>
<th>Description</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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<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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<tr>
<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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<tr>
<td>DOS</td>
<td>Density of states</td>
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<tr>
<td>FET</td>
<td>Field effect transistor</td>
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<tr>
<td>GeNW</td>
<td>Germanium nanowire</td>
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<tr>
<td>GGA</td>
<td>General gradient approximation</td>
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<tr>
<td>GULP</td>
<td>General utility lattice program</td>
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<tr>
<td>HF</td>
<td>Hartree-Fock</td>
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<tr>
<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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<tr>
<td>IPHT</td>
<td>Institute of Photonic Technology</td>
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<tr>
<td>IPR</td>
<td>Inverse participation ratio</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>I-V</td>
<td>Current voltage</td>
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<tr>
<td>KS</td>
<td>Kohn-Sham</td>
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<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
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<tr>
<td>LDA</td>
<td>Local density approximation</td>
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<td>MD</td>
<td>Molecular dynamics</td>
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<tr>
<td>NVE</td>
<td>Constant energy and constant volume</td>
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<tr>
<td>PAW</td>
<td>Projector augmented-wave</td>
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<tr>
<td>PDOS</td>
<td>Projected density of states</td>
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**PVCVD**  Plasma-enhanced chemical vapor deposition

**PPs**  Pseudopotentials

**PV**  Photovoltaics

**QR**  Quench rate

**RDF**  Radial distribution function

**RF**  Radio Frequency

**SCF**  Self-consistent field

**SFI**  Science Foundation Ireland

**SiNW**  Silicon Nanowire

**SR**  Spectral response

**SWE**  Staebler–Wronski effect

**TA**  Transverse acoustic

**TO**  Transverse optical

**VDOS**  Vibrational density of states

**VASP**  Vienna ab-initio simulation package

**VBM**  Valence band maxima
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 –NH₂ 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\textsuperscript{1} 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\textsuperscript{1}.

Focussing 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.](image-url)
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 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 point 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.](image)
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 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\textsuperscript{71,72,73,74,75,76,77} 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.\textsuperscript{77} 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\textsuperscript{71} 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\textsuperscript{72} 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 \textit{et al.}\textsuperscript{58} stated that the optical gap of a-Si:H depends on the H-content which is regulated by the H\textsubscript{2} 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.\textsuperscript{74} grew a-Si:H films with H\textsubscript{2} 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 H\textsubscript{2} pressures, which can indicate that a saturation of H-content is reached, although, similar to reference \textsuperscript{77}, 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.\textsuperscript{75} 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 SiH\textsubscript{2} species should continuously increase the gap. Viturro and Wieser\textsuperscript{76} studied a-Si:H up to 8.5 % H-content, with this regime showing an increase in the optical gap. However, compared to reference \textsuperscript{77} and later works, e.g. references. 74 and 75, 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.\textsuperscript{78,79,80}, points out that a hypersaturation of H will generate nanoscopic regions of c-Si in an a-Si:H matrix. Additionally, in references \textsuperscript{78-80} 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\textsuperscript{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\textsuperscript{2}, which has to be compared with the physical limit of 29\% conversion efficiency in a c-Si solar cell\textsuperscript{84}, the process to make the cell experimental is 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\textsuperscript{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\textsuperscript{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)\textsuperscript{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 cm²
with Voc = 729mV, j_sc = 39.5 mA/cm² and FF = 80.0%, presented in 2009². In mass
production, the best HIT cells have 21.6% conversion efficiency, leading to 19.0% module
efficiency².

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 heterointerface⁹⁰ 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 interface⁹⁰,⁹¹. 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
junction 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>
</tr>
</thead>
<tbody>
<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>PECVD</td>
<td>I-V</td>
<td>101</td>
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<td>PECVD</td>
<td>VFP</td>
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<td>0.01</td>
<td>ECVD</td>
<td>C-V</td>
<td>102</td>
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<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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<td>0.49</td>
<td>0.175</td>
<td>PECVD</td>
<td>SR simulation</td>
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<td>0.44</td>
<td>0.16</td>
<td>PECVD</td>
<td>CFSYS</td>
<td>104</td>
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<tr>
<td>n/f</td>
<td>0.06</td>
<td>PECVD</td>
<td>C-V</td>
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<tr>
<td>n/f</td>
<td>0.35</td>
<td>PECVD</td>
<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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<tr>
<td>n/f</td>
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<td>PECVD</td>
<td>Coplanar conductance</td>
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<tr>
<td>0.458</td>
<td>n/f</td>
<td>PECVD</td>
<td>CFSYS (p,i,n)</td>
<td>109</td>
</tr>
<tr>
<td>&gt; 0.25</td>
<td>n/f</td>
<td>PECVD</td>
<td>AFM</td>
<td>113</td>
</tr>
</tbody>
</table>

**Theoretical results**

<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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<td>0.32 - 0.42</td>
<td>0.08 - 0.26</td>
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<td>analytical calculation</td>
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<tr>
<td>0.36 ± 0.05</td>
<td>0.18 ± 0.05</td>
<td></td>
<td>analytical calculation</td>
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<tr>
<td>0.46 ± 0.05</td>
<td>0.14 ± 0.1</td>
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<td>AFORS-HET</td>
<td>112</td>
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<tr>
<td>0.36</td>
<td>n/f</td>
<td></td>
<td>TB</td>
<td>109</td>
</tr>
</tbody>
</table>
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 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 ΔE VBM. The discontinuity in this reference potential across the heterostructure interface is defined as ΔVstep. The valence band offset, ΔEv, is calculated as

\[ ΔE_{v}^{aSi-cSi} = ΔE_{v}^{aSi-cSi}_{BM} + ΔV_{step} \]

The conduction band offset is determined from ΔEv and the difference in bulk band gaps, ΔEg, as

\[ ΔE_{c}^{aSi-cSi} = ΔE_{g}^{aSi-cSi} + ΔE_{v}^{aSi-cSi} \]

According to reference 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. 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 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\textsuperscript{130}. 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\textsuperscript{131,132,133,134,135,136}. 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\textsuperscript{131}.

From the perspective of modifying the band gap of nanowires, the focus for both Si\textsuperscript{131,137,138,139} and Ge nanowires\textsuperscript{131,137,140} 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 focusing 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\(^{152a,152b}\), 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.

\[
F_i = m_i \ddot{a}_i = m_i \frac{d^2 r_i(t)}{dt^2} \quad i = 1, 2, 3...N
\]  

3.1
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.

$$\vec{F}_i = -\frac{dU}{dr_i}$$  \hspace{1cm} \text{(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, $\vec{a}_i$ 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\textsuperscript{153} leapfrog algorithm given by:

\begin{align}
\vec{r}(t + \delta t) &= \vec{r}(t) + \delta t \vec{v} \left( t + \frac{1}{2} \delta t \right) \hspace{1cm} \text{(3.3)} \\
\vec{v} \left( t + \frac{1}{2} \delta t \right) &= \vec{v} \left( t - \frac{1}{2} \delta t \right) + \delta t \vec{a}(t) \hspace{1cm} \text{(3.4)}
\end{align}
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)\textsuperscript{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\textsuperscript{154}. The Tersoff potential is modelled by a Morse-type pair potential, which allows a physical interpretation of the potential parameters\textsuperscript{154-156}. Tersoff continued to make minor adjustments to the functional format\textsuperscript{154-156}; the format employed in this research and presented here is that published in references\textsuperscript{156,157}. If one were to consider a system of atoms, the total potential energy of the
system, $U$, could be captured as the sum of the energy of the individual bonds in the system. The Tersoff potential\textsuperscript{156} represents this empirically with:

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

$$f_A \left(r_{ij}\right) = A_{ij} \cdot \exp(-\lambda_{ij} r_{ij})$$\hspace{1cm}3.6

$$f_R \left(r_{ij}\right) = B_{ij} \cdot \exp(-\mu_{ij} r_{ij})$$\hspace{1cm}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 $\lambda$ and $\mu$ for atoms $i$ and $j$.

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

$$b_{ij} = \chi_{ij} \cdot \left(1 + \rho_i^{ni} \cdot \xi_{ij}^{ni} \right)^{-1}$$\hspace{1cm}3.8

$$\xi_{ij} = \sum_{k \neq i,j} f_c(r_{ij}) \cdot \omega_{ik} \cdot g(\theta_{ijk})$$\hspace{1cm}3.9
\[ g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos(\theta_{ijk}))^2} \tag{3.10} \]

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\(^{154-158}\). 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.

\[
f_c (r_{ij}) = \begin{cases} 
1 & R_{ij} < r_{ij} \\
\frac{1}{2} + \frac{1}{2} \cdot \cos \left( \pi \cdot \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}} \right) & R_{ij} < r_{ij} < S_{ij} \\
0 & S_{ij} < r_{ij}
\end{cases} \tag{3.11}
\]

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.
## Parameters

<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>
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<td>43.5310</td>
</tr>
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<td>λ (1/Å)</td>
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<tr>
<td>µ (1/Å)</td>
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<td>β</td>
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</tr>
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<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>
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</tr>
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<td>R (Å)</td>
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</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, $\text{Vee}[\rho]$,

$$E[\rho] = T[\rho] + V[\rho] + \text{Vee}[\rho]$$ \hspace{1cm} 3.13

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

$$V[\rho] = \int v(r)\rho(r) \, dr$$ \hspace{1cm} 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 $R_{A}$,

$$v(r) = -\sum_{A} \frac{Z_{A}}{|r-R_{A}|}$$ \hspace{1cm} 3.15

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

$$E[\rho] = F[\rho] + \int v(r)\rho(r) \, dr$$ \hspace{1cm} 3.16

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

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

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

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 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.

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

Because the electrons in this fictitious system do not interact, the term $V_{ee}[\rho]$ vanishes, so the functional $F_{ks}[\rho]$ becomes simply
with the electron density given by

$$\rho(r) = \sum_{i=1}^{n} |\varphi_i(r)|^2$$  \hspace{1cm} (3.21)$$

Formally, $T_s[\rho]$ is a functional of the orbitals $\varphi_i$. 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

$$F[\rho] = T_{ks}[\rho] + U[\rho] + E_{xc}[\rho]$$  \hspace{1cm} (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

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

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

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

$$v_{ks}(r) = v(r) + v_{XC}(r) + v_H(r)$$  \hspace{1cm} (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 \( \rho(r) \)

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

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.

$$E_{xc}^{GG} = E_{xc}^{LDA} + F_{xc} \rho(r) \frac{\partial}{\partial r} \rho(r) dr$$

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
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:

![Diagram of self-consistent iterative solution of Kohn-Sham equations]

- **Initial Guess** \( \rho(r) \)
- **Calculate Effective Potential**
  \( v_{\text{eff}}(r) = V_{\text{en}}(r) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{\text{xc}}[\rho(r)] \)
- **Solve Kohn-Sham Equations**
  \( \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}} \right] \psi_i = \varepsilon_i \psi_i \)
- **Evaluate the Electron Density & Total Energy**
  \( \rho(r) = \sum_i |\psi_i(r)|^2 \quad \text{and} \quad E_{\text{tot}}[\rho(r)] = \ldots \)
- **Converged?**
- **Output Quantities**
  \( \rho_0(r), E_{\text{tot}}[\rho_0(r)] \rightarrow \text{Forces, Eigenvalues, ...} \)

Figure 3.1 Self-consistent Iterative Solution of Kohn-Sham equations.

### 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),

$$g(r) = \frac{1}{n(n-1)} dR_1 dR_2 dR_3 ... dR_n \sum_{i,j} \delta(|R_i - R_j| - 1)$$  \hspace{1cm} 3.30

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. 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. 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):

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

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$^{31}$. 

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First Principles Modeling of Hydrogenated Amorphous silicon  Page 54
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\textsuperscript{31, 165}.

![Figure 3.2](image)

Figure 3.2 The schematic representation of the distribution of density of allowed energy states for electrons for (a) single crystal silicon (b) \textit{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
\[ g(k) dE = \frac{a^3}{\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} dE \] 3.32

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\(^{31}\). 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 $\Psi_i(\bar{r})$

$$IPR_i = \frac{\int_V \left| \Psi_i(\bar{r}) \right|^4 d\bar{r}}{\left( \int_V \left| \Psi_i(\bar{r}) \right|^2 d\bar{r} \right)^2} \quad 3.33$$

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 \([\alpha(E)xE]^{1/2}\) plotted against the photon energy \(E\). Here \(\alpha(E)\) is the absorption coefficient which is calculated from

\[
\alpha = \frac{2\kappa\pi}{\lambda} \tag{3.34}
\]

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

\[
\kappa = \frac{1}{\sqrt{2}} \sqrt{-\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2 - \epsilon_1}} \tag{3.35}
\]

The variables \(\epsilon_1\) and \(\epsilon_2\) 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: 1x10\textsuperscript{12} K/s, 1.33x10\textsuperscript{12} K/s and 2x10\textsuperscript{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 \textit{ab initio} simulation package (VASP)\textsuperscript{175,176,177}. The generalized gradient approximation (PW91)\textsuperscript{178} to the exchange-correlation functional was applied. The interactions between ion cores and valence electrons are described using the projector-augmented wave method (PAW)\textsuperscript{179}, 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\textsuperscript{180}. 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\textsuperscript{181} functional, with 25% exact exchange and a screening length of 0.2 Å\textsuperscript{-1}, 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\textsuperscript{177}. 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\textsuperscript{181} 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) method¹⁷⁹, 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 Discharge¹⁸² produces the best quality material, although other more recent CVD methods¹⁸³,¹⁸⁴ 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 Searle¹⁸⁵ and Street.³¹

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.
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.

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
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 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 \((1 \times 10^{12} \text{ K/s})\) 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 \(4 \times 10^{14} \text{ K/s}\) (c) quench rate \(2 \times 10^{12} \text{ K/s}\) (c) quench rate \(1.3 \times 10^{12} \text{ K/s}\) (d) quench rate \(1 \times 10^{12} \text{ K/s}\) (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 of 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 350 K for 250 ps in the NVE ensemble, with an integration timestep of 0.1 fs and Verlet leapfrog integration\textsuperscript{153}. We quench to 300 K at three rates: 1x10\textsuperscript{12} K/s, 1.33x10\textsuperscript{12} K/s and 2x10\textsuperscript{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\textsuperscript{181}, with 25 % exact exchange and a 0.2 Å\textsuperscript{-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\textsuperscript{167}.
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 $1 \times 10^{12}$ K/s, $1.33 \times 10^{12}$ K/s and $2 \times 10^{12}$ 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 \textsuperscript{31} and \textsuperscript{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.

![Image](image_url)

(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) $1.0 \times 10^{12}$ K/s (b) $1.33 \times 10^{12}$ K/s and (c) $2.0 \times 10^{12}$ K/s.
There remains the question of the origin of the undeniable decrease of $E_{opt}$ by lowering the H concentration that is found experimental$^{71,72,76}$. To investigate the effect of H concentration on $E_{opt}$, 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 $E_{opt}$ (~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 $1\times10^{12}$ K/s, $1.33\times10^{12}$ K/s, and $2\times10^{12}$ 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>
</tbody>
</table>
Experimental Results

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>$E_{\text{mob}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cody et al., ref. 77</td>
<td>1.70 ±0.03</td>
<td>---</td>
</tr>
<tr>
<td>Lee et al., ref. 13</td>
<td>1.73 - 1.76</td>
<td>1.88 - 1.90</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 x10^{12} K/s and a 14.0 % hydrogen concentration in a-Si:H (b) a quench rate of 2 x10^{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}.
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\cite{78,79,80,166,67,23}, in particular for a-Si:H generated in references\cite{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\cite{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\cite{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.
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 and calculations on a-Si:H. 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. 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.](image)

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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.

![Graph showing the IPR for saturated and unsaturated a-Si:H structures around the Fermi level.](image)
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. 

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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 
occuring 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 \(^{78-80}\), 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 1x \(10^{12}\) 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 midly 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-Hₙ bonds, and the remainder is bonded forming Si-H₂ (4%) and Si-H₃ (1%). Si-Hₙ bonds have been observed experimentally from infrared spectroscopy¹⁹¹. The formation of lower number of Si-H₂ bonds is good indication good grade hydrogenated amorphous silicon¹⁹⁸.

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 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 \cite{13,15} and the impact of H content on the in $a$-Si:H around H saturation has been already discussed in reference \cite{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 \cite{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 \cite{63,73,75-77,190}.

Figure 5.4 Tetrahedral angle distribution for bulk $a$-Si and $a$-Si:H with different H content.
Figure 5.5 Tauc plots to obtain the optical band gap for H undersaturation in a-Si:H.

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 under saturated 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 showing mobility and optical band gap energies as a function of H concentration in a-Si:H.](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. 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 of Si-Si bond lengths for a-Si and a-Si:H with different H concentrations.](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’79 and Stuckelberger’s works200 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.
CHAPTER 6

6 Surface Orientation and Amorphous Layer Thickness Effects in Crystalline-Amorphous Silicon (a-Si:H/c-Si) Interfaces

6.1 Introduction

In this chapter we present the results of empirical potential and density functional theory (DFT) studies of models of interfaces between amorphous silicon (a-Si) or hydrogenated amorphous Si (a-Si:H) and crystalline Si (c-Si) on three unreconstructed silicon surfaces, namely (100), (110) and (111). a-Si:H/c-Si brings challenges in understanding factors such as surface orientation, the role of the interface region (band offsets and defect density), the amount of hydrogen needed to passivate the dangling silicon and the influence of hydrogen in electronic and optical properties. A better understanding of these challenges will improve a-Si:H/c-Si heterojunctions because these challenges influence device performance.

These atomic-scale simulations of the interfaces are aimed at clarifying several questions concerning the structural and electronic and optical properties of a-Si:H/c-Si heterojunctions and any dependence on the Si surface orientation and interface structure. We present herein a-Si:H/c-Si interfaces in which a-Si is formed from partially melted and quenched models of the (100), (110) and (111) Si surfaces.

The (100) surface is the least stable crystalline surface as measured by surface energy and forms the thickest amorphous Si region, while the most stable (110) surface forms the smallest amorphous region. Table 6.1 shows the melting time of different orientations of c-Si surfaces and the effect of melting time on proportions of amorphous and crystalline Si in (100), (110) and (111) oriented a-Si:H/c-Si interfaces. Calculated radial distribution
functions (RDF) in the amorphous and crystalline layers are consistent with a-Si or a-Si:H and c-Si and indicate a structural interface region one layer thick. The electronic density of states shows an evolution from c-Si

Table 6.1 Effect of melting time on proportions of amorphous and crystalline Si in (100), (110) and (111) oriented a-Si:H/c-Si interfaces.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Melting time (ps)</th>
<th>Hydrogenated a-Si layer thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>10</td>
<td>48%-a-Si:H-52%-c-Si</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>65%-aSi:H-35%-c-Si</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>82%-a-Si:H-18%-c-Si</td>
</tr>
<tr>
<td>(110)</td>
<td>10</td>
<td>13%-a-Si:H-87%-c-Si</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>34%-a-Si:H-66%-c-Si</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>56%-a-Si:H-44%-c-Si</td>
</tr>
<tr>
<td>(111)</td>
<td>10</td>
<td>26%-a-Si:H-74%-c-Si</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>47%-a-Si:H-53%-c-Si</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>58%-a-Si:H-42%-c-Si</td>
</tr>
</tbody>
</table>

to a-Si (or a-Si:H), with a larger electronic interface layer, suggesting that the electronic properties are more strongly perturbed by interface formation compared to the atomic structure. The computed optical absorption spectra show strong effects arising from the formation of different a-Si and a-Si:H regions on the c-Si surfaces. The optical gaps are sensitive to surface orientation and thickness of the amorphous region. Our model suggests a rational strategy to tune the light absorption properties in a-Si:H/c-Si solar cell structures based tuning the thickness of a-Si:H layer. We also present the valence and conduction band
offsets for different orientations and different thicknesses of the a-Si:H layer. From these results we conclude that thickness of the amorphous Si layer plays a great role in determining the valance and conduction band offset. The original Si surface orientation does not have significant impact on the magnitude of the valence or the conduction band offsets. In general, when the thickness of a-Si:H layers increase the valance and conduction band offset also increase and the valence band offset is saturated at 0.65 eV. The magnitude of the increase is different for the valence and conduction band offsets with amorphous thickness layers. This is because the thickness of the layers affects more the valence band edge than the conduction band edge.

6.2 Atomic structure of a-Si/c-Si interface models

We use a heat and quench approach to generate models of a-Si:H/c-Si, starting from unreconstructed, bulk terminated crystalline Si (100), (110) and (111) surfaces, using the classical molecular dynamics code GULP as discussed in chapter 3. The surfaces are (2 x 2) surface supercells and are bulk cleaved to have 512 atoms in (100) and (111) (32 layers) and 522 atoms in (110) (29 layers) to minimise the influence of the size of the surface model on formation of the amorphous region. Within a molecular dynamics framework, heat and quench is a very common approach for generating models of amorphous silicon. The Tersoff interatomic potential is used for Si and H. In the two dimensional periodic boundary condition MD simulations we run an initial “melting” simulation at 3000 K for 10 ps, 80 ps, and 200 ps in the constant volume and energy ensemble (NVE), using a simulation timestep of 0.1 fs. These 10 ps, 80 ps, and 200 ps simulations allow for some melting of the initially crystalline Si surface, while the extent of melting in the surface will depend on the surface stability (Section 6.3). The structure resulting from the 10 ps, 80 ps, and 200 ps simulations are subsequently quenched to 300 K at a rate of 6x10^{12} K/s. After quenching, the a-Si/c-Si
interfaces are annealed for 25 ps at 300 K. During preparation of a-Si/c-Si interfaces we need to be aware that at sufficiently long melting times every orientation of Si we study will produce a-Si.

Figure (6.1-6.3) (left panels) show the atomic structure of the relaxed non-hydrogenated a-Si/c-Si and the relaxed hydrogenated a-Si:H/c-Si models for the (100), (110) and (111) Si surfaces. Experimental and theoretical surface energy calculations\textsuperscript{201,202,203} indicate that for the bulk terminated unreconstructed surfaces considered in this work, the stability is as follows: (100) < (111) < (110). Upon examining the structures generated from an initial 10 ps melt simulation, the (100) surface has the largest amorphous region, with the most stable (110) surface displaying the smallest amorphous region. This is consistent with the stability of each surface found from the surface energies and suggests that the orientation of the Si surface can play a role in determining the relative thickness of an a-Si layer on c-Si.
Figure 6.1 Atomic structure and layer resolved radial distribution function of a-Si/c-Si and a-Si:H/c-Si interface models in the (100) Si surface. The labelling of the layers runs from B (crystalline) to M (amorphous). Si atoms are yellow spheres and H atoms are white. The black arrow indicates the interface region.
Figure. 6.2 Atomic structure and layer resolved radial distribution function of a-Si/c-Si and a-Si:H/c-Si interface models in the (110) Si surface. The labelling of the layers runs from B (crystalline) to M (amorphous). Si atoms are yellow spheres and H atoms are white. The black arrow indicates the interface region.
Figure 6.3 Atomic structure and layer resolved radial distribution function of a-Si/c-Si and a-Si:H/c-Si interface models in the (111) Si surface. The labelling of the layers runs from E (crystalline) to M (amorphous). Si atoms are yellow spheres and H atoms are white. The black arrow indicates the interface region.

In Figure 6.1–6.3 (right panels), the Si–Si radial distribution function (RDF) is shown in a layer-by-layer format in selected crystalline and amorphous layers, where a layer is defined as a region that is half the Si lattice constant. The RDF measures the local structure in a-Si and is experimentally accessible, providing a useful tool for comparing the computationally created structures with real samples. In crystalline materials, there are sharp peaks at the neighbouring, next neighbour etc. Si–Si distances, indicative of short and long range order. In amorphous Si, there is a peak at the nearest neighbour Si–Si distance, indicating short range order. The disorder present in a-Si means that the long range RDF peaks are broadened and coalesce, indicative of no long range order. In Figure 6.1–6.3, both the crystalline and
amorphous regions show RDFs that are typical of bulk crystalline and amorphous Si\textsuperscript{201}, with the a-Si layers showing no defined peaks indicating no long range order.

The apparent amorphous regions (layers I–M in (100), Figure 6.1; layer M in (110), Figure 2; layers L–M in (111), Figure 3) show a defined peak at the neighbouring Si–Si distance, with a reduced maximum and increased broadening in this peak compared with the crystalline RDF. The second and subsequent peaks are typical of amorphous Si.

Examining the RDF, we can also attempt to identify an interface region, which we term the structural interface. For (100), this can be considered to be in layer G, where it is clear that Si atoms are displaced from their lattice sites, when compared to layer B for example. For the (110) surface it is layer L and for (111) it is layer K. In these layers, while the RDF is obviously not characteristic of an amorphous region, it nonetheless is also not typical of crystalline Si and it is clear that the peak heights (the structures are less ordered than crystalline silicon and more ordered than amorphous silicon) are reduced and the peak widths (most of the structures have Si-Si distances distorted from c-Si in structures that are not fully ordered) are reduced and the peak widths are bigger, indicating that the interface region is intermediate between c-Si and a-Si and we find this interface to be one layer thick.

We have determined the number of undercoordinated (2 and 3-fold) and 5 coordinated Si in the a-Si region of the heterostructures. For (100), 11% of Si are not 4-fold coordinated, while in the (110) and (111) surfaces, 5% and 8% of Si atoms are not 4-fold coordinated. Interestingly, the total density of dangling and floating defects follows the inverse order to the surface stability of the various orientations (100) > (111) > (110).

We have added hydrogen (as discussed in Chapter 2) to passivate the dangling Si bonds in the a-Si layer and relaxed these a-Si:H/c-Si interfaces with DFT. Figures 6.1–6.3 show the
atomic structure of the relaxed a-Si:H/c-Si interfaces for the (100), (110) and (111) surfaces as well as the layer resolved RDF. On computing the Si coordination numbers, we find that the number of Si atoms that are not 4-fold coordinated are significantly reduced to 1.4%, 0.5% and 1% in (100), (110) and (111), yielding again higher density of coordination defects for the surfaces with lower stability but a notable reduction compared to the pure a-Si with no hydrogen.

The RDF for the a-Si:H/c-Si interface in the (100) surface can be compared with that of the non-hydrogenated surface (see Figure 6.1) and we find that the presence of hydrogen improves the order in the non-crystalline layers, as indicated by the coordination numbers, but the RDF of the interface region remains consistent with an amorphous structure. For the other surfaces, the inclusion of hydrogen also improves the order in the interface region. For example, for the (110) surface the presence of hydrogen leads to higher values of the first and second maximum of the RDF of layer L compared with the non-hydrogenated structures in Figure. 6.2. The reason for this is that including hydrogen increases the number of four-fold Si in the structure and therefore reduces the number of undercoordinated Si and strained Si–Si bonds. Finally, in the (111) surface, layer K is the interface layer, with an increase in short and medium range order, as indicated by the first two peaks in the RDF (Figure 6.3).
Figure 6.4 Atomic structure and layer resolved radial distribution function of a-Si:H/c-Si interface models in the (100) Si surface. The labelling of the layers runs from B (crystalline) to M (amorphous). Si atoms are yellow spheres and H atoms are white. The black arrow indicates the interface region. (a) 80 ps melting time (b) 200 ps.
Figure 6.5 Atomic structure and layer resolved radial distribution function of a-Si:H/c-Si interface models in the (110) Si surface. The labelling of the layers runs from B (crystalline) to M (amorphous). Si atoms are yellow spheres and H atoms are white. The black arrow indicates the interface region. (a) 80 ps melting time (b) 200 ps.
Figure 6.6 Atomic structure and layer resolved radial distribution function of a-Si:H/c-Si interface models in the (111) Si surface. The labelling of the layers runs from B (crystalline) to M (amorphous). Si atoms are yellow spheres and H atoms are white. The black arrow indicates the interface region. (a) 80 ps melting time (b) 200 ps.
We have further expanded our a-Si:H/c-Si interface work by including results from 80 and 200 ps melting time MD simulations. In figure 6.4(a and b)–6.6 (a and b) left panels show the atomic structure of the relaxed hydrogenated a-Si:H/c-Si models for the (100), (110) and (111) 80 and 200 ps melting simulation Si surfaces respectively. As we have discussed above the stability is in the order (100) < (111) < (110). The (100) surface has the largest amorphous region, with the most stable (110) surface displaying the smallest amorphous region. This is consistent with the 10 ps melting time simulation. The only difference we find is that for longest melting times, the stability of (111) is greater than (110) surface. We show in figure 6.4(a and b)–6.6 (a and b) right panels the Si-Si radial distribution function (RDF) in a layer-by-layer format that shows the RDF in each crystalline and amorphous layer for a-Si:H/c-Si models for the (100), (110) and (111) 80 and 200 ps melting stimulation respectively. In all calculations the amorphous regions show a defined peak at the neighbouring Si-Si distance, with a reduced maximum and increased broadening in this peak compared with the crystalline RDF. The second and subsequent peaks are typical of amorphous Si. These show that the amorphous region has only short range order interactions and the crystalline region has both long and short range order interactions. This is consistent with the results that we found from 10 ps simulations.

6.3 Electronic properties of a-Si:H/c-Si interfaces

a-Si:H and c-Si display different electronic properties as a result of their different structures. c-Si shows a clear valence band to conduction band energy gap and no states in the energy gap. a-Si:H shows the well known tail states and a larger energy gap than c-Si, which arises from the disorder present in a-Si:H\(^2\)\(^{204,66,69}\). Amorphous Si is characterised by the valence and conduction band mobility edges and the presence of electronic states around the Fermi level,
arising from the presence of undercoordinated Si, which are removed by incorporation of hydrogen as discussed in chapter 4 and 5.

To examine the electronic properties in the interface models, we show in Fig. 6.7 and 6.8 the total electronic density of states (EDOS) in the crystalline Si layers nearest the interface for 10 ps melting simulations for each orientation (not all c-Si layers are shown, since the EDOS is unchanged in the layers farthest away from the interface) through the interface and in the a-Si or a-Si:H layers in a 2-D stacked plot. Figure 6.7 shows the layer-by-layer EDOS in the non-hydrogenated a-Si/c-Si surfaces and Figure 6.8 shows the EDOS in the hydrogenated a-Si:H/c-Si surfaces.
Figure 6.7 Atomic structure and layered-resolved total electronic density of states (EDOS) plots for each unhydrogenated a-Si/c-Si interface structure. (a) (100) surface, (b) (110) surface, (c) (111) surface from 10 ps melt simulations followed by DFT relaxation. The EDOS for selected crystalline layers are shown (bottom plot), since the EDOS is invariant on going through the crystalline layers. The zero of energy is referenced to the Fermi level.
determined with VASP for the individual structures and we display valence band states to 2 eV below the Fermi level and conduction band states to 1 eV above the Fermi level.
Figure 6.8 Atomic structure and layered-resolved total electronic density of states (EDOS) plots for each a-Si:H/c-Si interface structure. (a) (100) surface, (b) (110) surface, (c) (111) surface from 10 ps melt simulations followed by DFT relaxation. The EDOS for selected crystalline layers are shown (bottom plot), since the EDOS is invariant on going through the crystalline layers. The zero of energy is referenced to the Fermi level determined with VASP for the individual structures and we display valence band states to 2 eV below the Fermi level and conduction band states to 1 eV above the Fermi level.

For the c-Si region, the EDOS shows a clear separation between the valence and conduction bands. When we go from crystalline region to amorphous there is a change in the nature of the EDOS. Taking first non-hydrogenated a-Si/c-Si interfaces, we see that in the (100) surface figure 6.8 (a), regions G and H already start to show a deviation from the c-Si EDOS to an EDOS characterised by formation of valence and conduction band tails, signifying the onset of disorder in these layers. By region I, a clear signature of a-Si in the EDOS is present,
namely in-gap states due to undercoordinated Si and the band tails. In the a-Si regions in each surface, the EDOS is non-vanishing at the Fermi energy. This originates from the characteristics of amorphous Si, primarily attributed to the existence of structural defects which arise from dangling bonds and long Si–Si (strained) bonds. Taken in general, the EDOS in the amorphous regions has the typical form of bulk a-Si and the EDOS in the crystalline regions is typical of bulk c-Si with an evolution of band tails apparently e.g. in regions.

For the (110) and (111) surfaces, the EDOS shows that the amorphous region extends over fewer layers compared to the (100) surface, consistent with the structural analysis. In the (110) and (111) surfaces, we see that in layers K the EDOS is already modified from that of c-Si and in region L and J, which were identified as the structural interface layer, the EDOS shows amorphous character.

In the hydrogenated a-Si:H/c-Si interfaces figure 6.8, the crystalline regions have a EDOS consistent with c-Si. Taking the (100) surface, with the largest amorphous region, regions G–J, display a EDOS that is consistent with less disorder in these layers compared to the non-hydrogenated interface as a result of hydrogen incorporation. This is characterised by the removal of the states around the Fermi level, with the band tails persisting. Regions K–M therefore display an EDOS consistent with bulk hydrogenated a-Si with an optimum hydrogen concentration that removes the defect-induced electronic states around the Fermi level. In the (110) and (111) surfaces, we find a similar change in the electronic properties as a result of hydrogen incorporation. Thus hydrogenation clearly removes disorder between a-Si/c-Si.

It is interesting to contrast the identification of any interface between the amorphous and crystalline regions from the structural and electronic information in our model a-Si/c-Si.
heterostructures. Using the RDF (structural), the interface between the two regions appears to be abrupt, being essentially over one layer. However, the EDOS would indicate that the interface region is spread over a larger region, with characteristics of disorder appearing in layers that display an RDF characteristic of crystalline silicon. On examining the structures, we can see that the layers displaying a modified EDOS (compared to c-Si) show Si atoms displaced off their lattice sites, but not to the extent seen in the a-Si and a-Si:H layers. However, the RDF in these layers is little changed from the c-Si layers and is less sensitive to small changes in the local atomic structure when compared to the EDOS. We suggest that an interface region can be best identified from analysis of the electronic density of states.
First Principles Modeling of Hydrogenated Amorphous silicon
First Principles Modeling of Hydrogenated Amorphous silicon
First Principles Modeling of Hydrogenated Amorphous silicon

(c)

(d)
Figure 6.9 Atomic structures and Layered-resolved total electronic density of states (EDOS) plots for each hydrogenated interface structure. (a), (b) and (c) 80 ps (100), (110) and (111) surface and (d) (e) and (f) 200 ps (100) (110) and (111) surface respectively. The EDOS for selected crystalline layers are shown (bottom plot), since the EDOS is invariant on going
through the crystalline layers. The zero of energy is referenced to the Fermi level determined with VASP for the individual structures and we display valence band states to 2 eV below the Fermi level and conduction band states to 1 eV above the Fermi level.

We have also further expanded our electronic properties of the a-Si:H/c-Si interface by including results from 80 and 200 ps melting time MD simulations. In figure 6.9 electronic density of states (EDOS) plots for each hydrogenated interface structure. (a), (b) and (c) 80 ps (100), (110) and (111) surface and (d), (e) and (f) 200 ps (100) (110) and (111) surface respectively. As we have discussed above the stability is in the order (100) < (111) < (110). The (100) surface has the largest amorphous region, with the most stable (110) surface displaying the smallest amorphous region. That means in the (110) and (111) surfaces, the EDOS shows that the amorphous region extends over fewer layers compared to the (100) surface, this is consistent with 10 ps melting time MD simulations.

6.4 Optical Properties of a-Si:H/c-Si interfaces

The optical properties of the hydrogenated amorphous-crystalline silicon interface are important because they can allow increased light absorption in the visible region. This increases the number of photogenerated carriers (holes and electrons) in the solar cell, enhancing efficiency.
Figure 6.10 Computed optical absorption spectra for the a-Si/c-Si and a-Si:H/c-Si interface models. (a) (100), (b) (110) and (c) (111) arising from different heat and quench melting time.

Figure 6.10 (a)-(c) shows the absorption spectra for the three surface orientations of a-Si:H/c-Si, each with three different a-Si:H thicknesses. Taking the (100) surface orientation, figure 6.10 (a) shows an increase in light absorption in the low energy region with an increase in the thickness of the amorphous layer. Comparing the (110) and (111) interfaces, these interfaces show different spectra with respect to the (100) surface. This arises since the (100) surface, being least stable, produces the thickest amorphous region for the same growth conditions and so the absorption spectrum in this case looks like that of a-Si:H. The other surfaces
produce thinner amorphous regions, and the thinnest amorphous region gives a spectrum that is closely similar to that of c-Si (direct gap contribution). As the amorphous region gets thicker in the (110) and (111) orientations, the absorption spectrum changes, becoming more amorphous-like.

The optical properties of a-Si:H is also characterised by its value of the optical band gap, which is obtained from the spectra in figure 6.11 (a)-(c) by extrapolating the linear part of the spectrum, the well-known Tauc plot; optical gaps from Tauc plots are given in Table 6.2. The optical band gap of the (100) surface orientation is obtained by extrapolation, but the (110) and (111) surfaces require us to plot the individual contributions (amorphous and crystalline part) and make a linear combination of the individual optical band gaps weighted by their layer thickness to obtain the optical band gap of the interface. This is shown for an example interface in figure 6.11 (a)-(c), for which the linear combination of the amorphous and crystalline optical gaps gives an optical gap of 1.96 eV for this interface.

\[
E_{\text{opt}}(a\text{Si}:\text{H} - c\text{Si}) = \frac{\text{thickness of } a\text{Si}:\text{H}}{\text{total thickness}} \times E_{\text{opt}}(a\text{Si}:\text{H}) + \frac{\text{thickness of } c\text{Si}}{\text{total thickness}} \times E_{\text{opt}}(c\text{Si}) \quad 6.1
\]
Figure 6.11  Computed optical absorption spectra for different a-Si:H/c-Si interface models: (a) shows the absorption for the (110) orientation with 34%-aSi:H-66%-cSi and parts (b) and (c) show the decomposed absorption spectra for the amorphous and crystalline regions.

All surface orientations show a reduction in the optical band gap as the size of the amorphous region increases, tending towards that of bulk a-Si:H. Optical gaps from the (100) interfaces are smaller than those for other surface orientations. This is due to the fact that the (100) interface contains the thickest amorphous silicon layer. The (110) orientation interface with
composition 13%-a-Si:H-87%-c-Si a-Si:H/cSi gives the closest optical (direct) band gap to that of crystalline silicon (2.3 eV), which arises from having the thinnest amorphous silicon region.

In conclusion the first principles results of the optical band gap of amorphous-crystalline silicon interfaces show optical gaps that are sensitive to surface orientation and thickness of the amorphous region. Our model suggests a rational strategy to tune the light absorption properties in a-Si/c-Si solar cell structures based on structural properties.

Table 6.2 Computed optical band gaps for a-Si:H/c-Si interfaces. Since there are direct gaps, that is for pure c-Si is 2.30 eV and pure a-Si:H is 1.27 eV.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Hydrogenated a-Si layer thickness</th>
<th>Optical band gap E_{opt} (eV)</th>
<th>Number of dangling atom at the interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>48%-a-Si:H-52%-c-Si</td>
<td>1.74</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>65%-a-Si:H-35%-c-Si</td>
<td>1.60</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>82%-a-Si:H-18%-c-Si</td>
<td>1.30</td>
<td>2</td>
</tr>
<tr>
<td>(110)</td>
<td>13%-a-Si:H-87%-c-Si</td>
<td>2.23</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>34%-a-Si:H-66%-c-Si</td>
<td>1.96</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>56%-a-Si:H-44%-c-Si</td>
<td>1.70</td>
<td>4</td>
</tr>
<tr>
<td>(111)</td>
<td>26%-a-Si:H-74%-c-Si</td>
<td>2.14</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>47%-a-Si:H-53%-c-Si</td>
<td>1.81</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>58%-a-Si:H-42%-c-Si</td>
<td>1.61</td>
<td>3</td>
</tr>
</tbody>
</table>

We have also studied the a-Si:H/c-Si interface defects: during a-Si:H formation on a c-Si surface, the c-Si surface should make bonds to Si atoms of the a-Si film. However, dangling bonds can form at the a-Si:H/c-Si interface that lead to recombination active states in the
band gap at the interface. Similarly to the situation in the a-Si:H bulk, this will happen if the a-Si:H network configuration in the vicinity of a c-Si surface atom does not allow for the formation of a Si-Si bond. Just like in the a-Si:H bulk, also c-Si surface dangling bonds can be passivated by hydrogen. In our study we find that the amount of dangling silicon formation along the interface region is depending on the the surface orientation. We shown this in table 6.2. The (100) surface creates the least dangling Si bonds and (111) creates the most dangling Si bonds. Using (100) surface of c-Si is the key issues to obtaining low defect density a-Si:H/c-Si interfaces.

6.5 Band offsets between Amorphous/Crystalline Silicon Interfaces by Amorphous Layer Thickness

The performance of the heterojunction solar 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 low density of defect states at the interface. Experimentally the density of interface states can be modified by a pre-treatment of the Si wafers which results in different defect state densities at the amorphous/crystalline interface\textsuperscript{115} or by passivating the defects by deposition of a thin undoped a-Si:H buffer layer prior to the a-Si:H emitter deposition.

We have calculated band offsets of a-Si:H/c-Si heterojunctions and we discuss the influence of different surface orientations, of the amorphous layer thickness, and of the a-Si:H/c-Si interface defect state on the offsets and implications for device performance.
Figure 6.12 (a) determining $\Delta E_V$ (VB offset) and $\Delta E_c$ (CB offset) of interfaces model. For a-Si:H we use mobility edges. For c-Si we use VB and CB. The valence and conduction band offsets of (100) a-Si:H/c-Si interface of (100) orientation with 80 ps simulation melting
(b) Electrostatic potential of a-Si:H/c-Si interface to get $\Delta V_{\text{step}}$ to allow a-Si, c-Si VB and CB to align.

We have calculated the band offsets by two different techniques. First one is by using average electrostatic potential (see detail in Chapter 2). The second one is calculated directly from density of states and IPR. That means we have calculated the total DOS of a-Si:H/c-Si interface structure afterward splitting crystalline DOS from total DOS then finally calculating the valence and conduction band offsets by computing the difference in valence and conduction band edge of crystalline silicon and the corresponding mobility edges in a-Si:H respectively. Figure 6.13 (a) and (b) show the obtained valence and conduction band offsets of (100), (110) and (111) orientations of different amorphous layer thicknesses of a-Si:H/c-Si interfaces using electrostatic potential. From these results we investigate that different thicknesses of the layers of amorphous Si have a leading role in determining the valence and conduction band offset. In general, when the thickness of the a-Si:H layer increases the valence and conduction band offsets also increase. 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. Figure 6.13 (a) shows that the value of the valence band offset of 200 ps layer thickness of (100), (110) and (111) orientations is converged to 0.65 eV so that this can be compared to bulk a-Si/c-Si interfaces used in experiment that are 0.32 - 0.66 eV.

It is interesting to consider the influence of this band offset on charge carrier transport in heterojunction cells. The band offsets at the interface have a substantial influence on the solar cell characteristics and lead to several consequences for charge-carrier transport and recombination in heterojunction devices: large band offsets can hinder charge carrier transport over the heterojunction interface; because the charge carrier has to overcome the
band offset barrier. This reduces the charge collection at one of the contacts. Depending on the details of charge distribution and recombination at the heterointerface, this can manifest in the solar cell characteristics as an effect on I-V curve\textsuperscript{90, 205}. On the other hand, the band offset should not be too low: below a certain value of band offset the voltage ($V_{oc}$) of the device decreases substantially\textsuperscript{206}. At the same time, the minority charge carriers in the vicinity of the contact are hindered by the band offsets in the heterojunctions to reach the cell contacts, and thereby recombination at the contacts is effectively suppressed. Thus, low short circuit currents and high open circuit voltages ($V_{oc}$) can be expected in the cell. So we know that from our band offsets results, band offsets depend on the amorphous layer thickness. By controlling the amorphous layer thickness we can potentially optimise the solar cell parameters and improve solar cell performance.

To investigate the effect of surface orientation on band offset, we have prepared the same amorphous/crystalline percentages (48\%-%a-Si:H-52\%-%c-Si) of (100) and (111) surfaces of a-Si:H/c-Si interface. Using the average electrostatic potential technique the valence band offsets are 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.
Figure 6.13 The valence and conduction band offsets of a-Si:H/c-Si interface (a), (b) using electrostatic potential (c) and (d) Calculated by splinting the amorphous and crystalline density of states from total EDOS.
6.6 Conclusions

In this work, interface models of amorphous–crystalline silicon are 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 with the highest density of coordination defects, while the most stable (110) surface forms the smallest amorphous region with the least defects. Analysis of the RDF indicates a structural interface region one layer thick in both a-Si/c-Si and a-Si:H/c-Si interfaces. In a-Si/c-Si, the electronic density of states shows new electronic states forming as a result of disorder, even in the seemingly crystalline layers, since the EDOS is more sensitive to small perturbations in the atomic positions from their perfect lattice sites than is the RDF, so that the use of the RDF alone to identify an interface region is not sufficient. The a-Si layers show a EDOS typical of bulk a-Si. Addition of hydrogen to the a-Si region changes the DOS in a similar fashion to bulk a-Si, due to passivation of dangling silicon atoms. 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. These results provide a useful starting point to further analyse the properties of a-Si/c-Si heterostructures prepared with different thicknesses of amorphous silicon, which is important for understanding and optimising the light absorption and charge dynamics of a-Si/c-Si solar cell heterostructures. In conclusion amorphous-crystalline silicon interfaces show optical gaps that are sensitive to surface orientation and thickness of the amorphous region. Our model suggests a rational strategy to tune the light absorption properties in a-Si/c-Si solar cell structures based on structural properties.
We calculated for the first time band offsets of a-Si:H/c-Si heterojunctions big system from first principle and examined the influence of different surface orientations and of the amorphous layer thickness and of a-Si:H/c-Si interface defects on the offsets and implications for device performance. The band offsets at the interface have a substantial influence on the solar cell characteristics and lead to several consequences for charge-carrier transport and recombination in heterojunction devices. The band offsets depend on the amorphous layer thickness and increasing with thickness. By controlling the amorphous layer thickness we can potentially optimise the solar cell parameters. We investigate the effect of surface orientation on interface defect states. In our study we find that the amount of dangling silicon formation along the interface region is depending on the surface orientation. (100) and (111) surface orientations create the least and the most dangling silicon in the interface region, respectively. But the effect of orientation on offsets is not significant.
CHAPTER 7

7 Amorphous core/crystalline silicon shell silicon nanowires and Germanium nanowires

7.1 Amorphous core/crystalline shell silicon nanowires

7.1.1 Introduction

Si nanowire (Si NW) solar cells have been demonstrated with the potential to overcome the limitation of conventional planar silicon cells. Excellent light absorption can be achieved especially in the high energy region. Moreover, low-quality Si wafers can be used for these structures. SiNW arrays with so-called a-Si/c-Si core-shell structures, where two structures are interfaced, provide a p-n junction interface and efficient charge separation and collection, which improves device efficiency. Our experimental collaborators from Prof Fritz Falk’s group in The Institute of Photonic Technology (IPHT) Jena, Germany have demonstrated core-shell crystalline/amorphous (c-Si/a-Si:H) nanowire solar cells with record efficiencies of 7.29%\textsuperscript{22} and lately up to 10.00%\textsuperscript{18}.

Our final activity on the generation of atomic structural models has been to generate core-shell crystalline-amorphous Si nanowires, and comparing with results from planar interfaces. The Si nanowire model is oriented along the (100) direction, has a diameter of 5nm (which is the limit of the available computing resources), 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, figure 7.1 (a), which based on our analysis in chapter 6, suggests that during melting simulations, thicker disordered regions could form at the (100) facets than at the (111) facets.
Similar to the planar interfaces, we use molecular dynamics to generate core-shell silicon nanowires by partial melting of a crystalline SiNW and quickly quenching to trap the amorphous-crystalline core-shell structures, which is then characterized by its structural properties (radial distribution functions, coordination number distribution, Si-Si distance distribution) for all model structures. Electronic and optical properties are described for one of the core-shell structures shown in figure 7.1 (b). One reason for this is that our model structures have large 5nm diameter and it takes significant computational time to optimize the 960 atom and hydrogen structures 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 found 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 exploded and after a quench never relax to any kind of useful structure. Due to the above reasons we have present initial results of core-shell nanowires which nonetheless are a very useful next step in research activities on the core-shell NWs.

7.1.2 Structural analysis of different amorphous shell thickness in a-Si/c-Si NWs

Different simulation times at a temperature of 3000 K were investigated, since there is no existing information on simulating the formation of amorphous regions in these nanostructures. Figure 7.1 (b-f) shows the structures taken from MD simulation at 3000 K for the different melting times shown and then quenching to 300K and annealing 300K for 50 ps (see table 7.1). The structure is further relaxed using DFT. From this figure, we see that the (100) facets on the nanowire start to melt first at 50ps, while the (111) facets are more resistant to melting. In figure 7.1 (b and c) the (111) the facets show smaller regions of disorder than the (100) facets. After a 250 ps melt simulation, we can see that now the (111)
facets start to show disorder, figure 7.1 (d-f). This is entirely consistent with our findings for the planar surfaces and the known surface energies (and hence stability) of the corresponding bare Si surfaces. Finally at 450 ps an amorphous SiNW is obtained.

Table 7.1 Different melting times of a silicon nanowire and the corresponding structure is showed in figure 7.1.

<table>
<thead>
<tr>
<th>Melting time (ps)</th>
<th>Structure of SiNW in figure 7.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>a - Crystalline</td>
</tr>
<tr>
<td>50</td>
<td>b – a-Si/c-Si</td>
</tr>
<tr>
<td>150</td>
<td>c – a-Si/c-Si</td>
</tr>
<tr>
<td>250</td>
<td>d – a-Si/c-Si</td>
</tr>
<tr>
<td>350</td>
<td>e – a-Si/c-Si</td>
</tr>
<tr>
<td>450</td>
<td>f – amorphous</td>
</tr>
</tbody>
</table>

The corresponding RDFs are shown in figure 7.2. The amorphous regions of the nanowires are not uniform around the crystalline shell region so it is hard to assign layers in a similar fashion to the planar interfaces. For this reason we have only calculated RDFs of the total amorphous and the crystalline regions of the nanowires. In figure 7.2 (a) we observe that similar to bulk silicon, the c-Si NW RDF has both long and short range order. The RDF is shown in figure 7.2 (b-e) for different amorphous layer thickness a-Si/c-Si nanowires and figure 7.2 (f) for a-Si NW. The red line graph shows the RDF for the amorphous region and the black line shows the RDF for the crystalline region of the nanowires. The amorphous RDF shows a defined peak at the first maxima and distorted second maximum of g(r). That is typical behaviour of amorphous silicon and consistent with experiment and the bulk.
RDF presented in chapters 4-5 and references\textsuperscript{67, 199}. When we compare the RDF of pure crystalline NWs shown in figure 7.2 (a) and core crystalline nanowires in figure (b-e); both have short and long range order however, the long range core crystalline nanowires show broadening of all peaks especially in figure 7.2 (c-e). This is interpreted as the presence of amorphous NWs perturbing the crystalline NWs structures.
Figure 7.1: (a) Model of the crystalline (100) oriented 5 nm diameter Si nanowire (b-e) are different amorphous layer thickness of a-Si/c-Si core-shell nanowires and (e) amorphous Si nanowire.

Figure 7.2 Radial distribution function of (a) crystalline NW (b-e) different amorphous layer thickness of a-Si/c-Si NWs and (f) a-Si NW. Red line (amorphous) & Black line (crystalline)
Figure 7.3 shows the distribution of coordination numbers found in the a-SiNW structure and for different amorphous layer thickness of NWs. We found that with the thinnest amorphous layer there is already a significant proportion of dangling silicon. When we increase the size of the amorphous shell region of the nanowires the number of dangling Si (2 and 3 coordinated atoms) as well as the distortion of bonds (see figure 7.4) increases; this is due to the fact that the amorphous region of the structure is larger. a-Si NW contains the highest number of defect states make up from both dangling silicon and distorted Si-Si bonds (i.e. in this structure we need take into account that the number of dangling silicon is included the unpassivated Si surface atoms.

Figure 7.3 Coordination number distribution for a-Si nanowire and a-Si/c-Si nanowire with different amorphous layer thickness. b-f in the legend refer to structures in Table 7.1.
Figure 7.4 Distribution of Si-Si-bond lengths for a-Si nanowire and a-Si/c-Si nanowire with different amorphous Si layer thickness.

We also present a detailed structural description of the Si-Si bond length distribution of a-Si NW with different layer thickness of a-Si/c-Si NWs, which is shown in Figure 7.4. The 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. The distribution function of the core-shell NW in figure 7.1 (b) shows a sharp peak at around 2.34 Å, with the least distorted Si-Si bonds. The core-shell structures with large a-Si regions increase the distortion in the peak at around 2.34 Å and number of strained Si bonds, that is Si-Si distances > 2.4 Å. In chapter 5 The Si-Si bond distribution of a-Si shows notable deviations from the perfect tetrahedral network and a bond length distribution that extends to Si-Si distances longer than 2.4 Å. When we compare the Si-Si strained bonds of a-Si nanowires with Bulk a-Si, the nanowire has less strained bonds than bulk a-Si. This has a potential advantage to reduce the presence of gap states as well as the band tails which are contributed by the strained Si-Si bond.
7.1.3 Structural properties of a-Si/c-Si and a-Si:H/c-Si nanowire

In this section we focus on one of the fully relaxed a-Si:H/c-Si NW, that is shown in figure 7.5 and the corresponding RDF for the amorphous region is presented in figure 7.6. As we expect hydrogenated nanowires have better-defined RDF peaks in the short range than a-Si region NW, e.g. in the tail of the first peak.

![Structural model](image1)

(a) (b)

Figure 7.5 Structural model of (a) a-Si/c-Si (b) a-Si:H/c-Si nanowires after DFT relaxation.

![Radial distribution function](image2)

Figure 7.6 Radial distribution function of (a) a-Si/c-Si NWs and (b) a-Si:H/c-Si NW.
The coordination number distribution of a-Si/c-Si and a-Si:H/c-Si is shown in figure 7.7. In a-Si:H/c-Si 2 co-ordinated Si disappear and the number of 3 and 5 co-ordinated Si are reduced compared to a-Si/c-Si NW. Almost all the remaining 3 and 5 co-ordinated Si raise from surface atoms of the nanowire.

![Graph showing coordination number distribution](image)

Figure 7.7 Coordination number distribution for a-Si nanowire and a-Si/c-Si nanowire with different amorphous layer thickness.

We have also calculated the average coordination number of a-Si/c-Si NW and its value is 3.54 and this value increases with the addition of hydrogen for a-Si:H/c-Si NW. The value, 3.76 is quite close to the experimental and our bulk coordination number value of bulk a-Si, 3.88 and 3.92 respectively. The lower value of the average coordination for both a-Si/c-Si and a-Si:H/c-Si NW compared to bulk a-Si:H arises from surface Si that are uncoordinated. These could be further passivated with a surface terminating group. e.g. halogen or OH as known for crystalline NWs.\(^{137,139,148,207}\).
Figure 7.8 Distribution of Si-Si-bond lengths of a-Si/c-Si and a-Si:H/c-Si nanowire.

The Si-Si distance distribution in a-Si/c-Si and a-Si:H/c-Si NWs is shown in figure 7.8. The presence of hydrogen in a-Si:H/c-Si NWs gives a sharper peak at around 2.34 Å than unhydrogenated a-Si/c-Si. The strained Si-Si bonds > 2.4 Å bonds which are present in a-Si/c-Si NW are reduced by addition of hydrogen as is clear from the tail in the plot in figure 7.8. This means the presence of hydrogen in the amorphous region in addition to killing the dangling silicon is also useful to reduce the distortions in the Si-Si bonds in the a-Si region. This result is consistent with what we find in bulk and interface models of a-Si.

7.1.4 Electronic and optical properties of a-Si/c-Si and a-Si:H/c-Si nanowires

The electronic structures of a-Si/c-Si and a-Si:H/c-Si NWs are determined from the final DFT relaxed structures, from which we extract an electronic density of states (DOS). As we can see in figure 7.9, the DOS shows no band gap, with a finite DOS around the Fermi level. The unrelaxed structure shows a significant density of states in the gap region. With DFT
relaxation and addition of hydrogen we have achieved a significant reduction extent of electronic in the states in the gap regions. Even if the hydrogenated NW has a finite density of states, this can also arise from the presence of undercoordinated Si atoms in the NW surface, but this is an interesting area for further exploration.

![Graph showing DOS for different configurations](image)

Figure 7.9 Total DOS for a-Si NW, a-Si/c-Si SiNW and a-Si:H/c-Si NW. The Fermi level is shifted to 0 eV.
Figure 7.10 (a) Optical absorption spectrum for a-Si/c-Si and a-Si:H/c-Si (b) Tauc plot and linear fit for the optical gap for a-Si/c-Si and a-Si:H/c-Si nanowires from 50 ps melt simulation.

Figure 7.8 (a), (b), shows the optical absorption and the linear extrapolation to determine the optical band gap of a-Si/c-Si and a-Si:H/c-Si NWs. For a-Si/c-Si NW, the optical gap is 1.30 eV and addition of hydrogen increases this gap to 1.41 eV. The optical gap of the a-Si/c-Si and a-Si:H/c-Si NWs are larger than bulk a-Si:H (1.25 eV). The main reason for this is due to quantum confinement in the SiNW structures, which gives a band gap increase compared to bulk as wire diameter decreases and is apparent for a 5 nm diameter NW.
7.2 Modifying the band gap of Germanium nanowires by surface termination

7.2.1 Introduction

Semiconductor nanowires, based on germanium (Ge) are potential candidates for many ICT applications, including next generation transistors, optoelectronics, gas and biosensing and photovoltaics. Key to these applications is the possibility to tune the band gap by changing the diameter of the nanowire. Ge nanowires of different diameter have been studied with H termination, but, using ideas from chemistry, changing the surface terminating group can be used to modulate the band gap. In this section we apply GGA-DFT and hybrid DFT approaches to study the effect of diameter and surface termination using –H, -NH₂ and –OH groups on the band gap of (001) oriented germanium nanowires.

In this section we examine different surface terminating chemical groups, -H, -OH and –NH₂ on GeNW of (100) orientation and different diameter and show how the diameter and surface termination determine the magnitude and nature of the nanowire band gap and also examine the influence of diameter and surface termination on the absorption spectrum of the nanowires. In this study, we use the generalised gradient approximation to DFT (GGA-DFT) and hybrid DFT (screened exchange HSE06 functional) to compute the band gaps and absorption edge for the different diameter Ge nanowires (10, 14 and 17 Å) with three different surface terminating chemical groups, -H, -OH and –NH₂.

We show that the surface terminating group allows both the magnitude and the nature of the band gap to be changed. We further show that the absorption edge shifts to longer wavelength with the –NH₂ and –OH terminations compared to the –H termination and we trace the origin of this effect to valence band modifications upon modifying the nanowire with –NH₂ or –OH.
These results show that it is possible to tune the band gap of small diameter Ge nanowires over a range of ca. 1.1 eV by simple surface chemistry. We also investigate the optical properties of the Ge nanowires through the absorption coefficient, $\alpha (E)$.

7.2.2 Structural Analysis of Ge Nanowires with Different Terminal Groups

For all GeNW, the initial atomic structure is constructed from diamond structured bulk Ge, by selecting all the Ge atoms that fall within a virtual cage placed around bulk Ge, while Ge atoms falling outside this virtual cage are removed. The surface dangling bonds were terminated with different terminal groups at full coverage, that is -H, –NH$_2$ and –OH, to form Ge-H, Ge-N and Ge-O bonds, with starting bond lengths of 1.56 Å, 1.92 Å and 1.84 Å respectively. The aim of the surface terminating groups is to maintain the original tetrahedral bond angles and to prevent surface reconstructions that would otherwise be present upon relaxation of a structure with dangling Ge present at the surface. We construct all of the GeNWs with a square cross-section.

Figure 7.11 (a – c) shows the atomic structure of Ge nanowires with 17 Å diameter and terminated by the three different terminating groups, namely –H (H is indicated by gray spheres), –NH$_2$ (N is indicated by blue spheres) and -OH (O is indicated by red spheres). Figure 7.12, 7.13) shows the atomic structures of Ge nanowires with 10 Å and 14 Å diameter with these terminal groups.

We consider firstly the effect of surface termination on the Ge-Ge bond distances, which are shown in table 7.2, with a particular emphasis on the difference between Ge-Ge distances in the core region, which have no bonding to the surface terminating group, and the Ge-Ge distances on the surface, which directly bind to the surface terminating group. Taking firstly the –H terminated 17 Å diameter nanowires, the Ge-Ge distances in the core region are 2.48
Å and in the surface the Ge-Ge distances are 2.47 Å; there is thus little difference between the bonding geometry in the core and surface regions for H-terminated nanowires, irrespective of the nanowire diameter.  

Figure 7.11: Atomic structure of 17 Å Germanium nanowire oriented along the (100) direction with different surface terminating groups: (a) –H (white gray = H), (b) –NH₂ (deep blue = N) and (c) -OH (red = Oxygen).

Figure 7.12: Atomic structure of 14 Å Germanium nanowire oriented along the (100) direction with different surface terminating groups: (a) –H (white gray = H), (b) –NH₂ (deep blue = N) and (c) -OH (red = Oxygen).
Figure 7.13: Atomic structure of 10 Å Germanium nanowire oriented along the (100) direction with different surface terminating groups: (a) –H (white gray = H), (b) –NH$_2$ (deep blue = N) and (c) -OH (red = Oxygen).

In the case of the -OH terminating group, the Ge-Ge distances in the core region and at the surface are quite different. The Ge-Ge distance of 2.52 Å at the surface of the largest diameter nanowire is notably longer than the Ge-Ge distance of 2.47 Å in the core region, with a similar difference persisting for the other nanowire diameters. Finally, the effect of the NH$_2$ terminating group lies between the –H and –OH terminations, reducing the surface Ge-Ge distances to 2.46 Å with the core Ge-Ge distances being 2.48 Å. It is clear that the interaction of surface Ge with oxygen has a much stronger effect on the local atomic structure than the interaction of Ge with the other surface terminating groups. The trends in the Ge-Ge core and surface distances for the 10 and 14 Å nanowires are the same as the 17 Å diameter nanowires for each surface termination.
Table 7.2: Relaxed Ge-Ge bond lengths, in Å, in the core and surface regions of the Ge nanowires.

<table>
<thead>
<tr>
<th></th>
<th>Diameter (Å)</th>
<th>Bond length (Å)</th>
<th>Diameter (Å)</th>
<th>Bond length (Å)</th>
<th>Diameter (Å)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (-H)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-Ge (surface)</td>
<td>10</td>
<td>2.46</td>
<td>14</td>
<td>2.46</td>
<td>17</td>
<td>2.47</td>
</tr>
<tr>
<td>Ge-Ge (core)</td>
<td>10</td>
<td>2.47</td>
<td>14</td>
<td>2.48</td>
<td>17</td>
<td>2.48</td>
</tr>
<tr>
<td>Ge-H</td>
<td></td>
<td>1.52</td>
<td></td>
<td>1.53</td>
<td></td>
<td>1.53</td>
</tr>
<tr>
<td>Amino (-NH₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-Ge (surface)</td>
<td>10</td>
<td>2.47</td>
<td>14</td>
<td>2.46</td>
<td>17</td>
<td>2.46</td>
</tr>
<tr>
<td>Ge-Ge (core)</td>
<td>10</td>
<td>2.49</td>
<td>14</td>
<td>2.49</td>
<td>17</td>
<td>2.48</td>
</tr>
<tr>
<td>Ge-N</td>
<td></td>
<td>1.91</td>
<td></td>
<td>1.92</td>
<td></td>
<td>1.92</td>
</tr>
<tr>
<td>Hydroxyl (-OH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-Ge (surface)</td>
<td>10</td>
<td>2.51</td>
<td>14</td>
<td>2.52</td>
<td>17</td>
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<td>14</td>
<td>2.48</td>
<td>17</td>
<td>2.48</td>
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<tr>
<td>Ge-N</td>
<td></td>
<td>1.84</td>
<td></td>
<td>1.85</td>
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<td>1.86</td>
</tr>
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7.2.3 Electronic Properties of Surface Modified GeNWs

In this section, we describe the band gap of Ge nanowires with different diameters and terminal groups, calculated using GGA-PBE and HSE06 to examine the dual effects of nanowire diameter and surface termination on the nature and the magnitude of the band gap. Bulk Ge has an experimental, indirect band gap of 0.74 eV\textsuperscript{209}. Theoretical calculations using several techniques have led to band gaps of Ge in the ranges of ~0.02 to 0.35 eV for LDA and GGA and hybrid DFT calculations reported an indirect gap in the range 0.63–0.77 eV\textsuperscript{210}. 
Thus, local DFT functionals underestimate the band gap, whereas band gaps from hybrid DFT are closer to the experimental results.

Figures (7.14 – 7.16) show the computed GGA-PBE band structures for the –H, -OH and -NH₂ terminated Ge nanowires of 10 Å (Figure 7.14), 14 Å (Figure 7.15) and 17 Å (Figure 7.16) diameter. The valence-conduction band gaps (and their nature, either direct or indirect) are shown in table 7.3. For a given terminating group the quantum confinement effect is clearly observed, with the smallest diameter nanowire having the largest band gap for all surface terminations. For –H, -NH₂ and –OH terminated nanowires the band gap reduces by 1.6 eV, 1 eV and 0.8 eV as the diameter changes from 10 Å to 17 Å respectively.

Figure 7.14: One-dimensional GGA-PBE band structure for (100)-oriented Germanium nanowires with -H termination. The Germanium nanowire diameters are 10 Å in part (a), 14 Å in part (b) and 17 Å in part (c).
Figure 7.15: One-dimensional GGA-PBE band structure for (100)-oriented Germanium nanowires with –NH₂ termination. The Germanium nanowire diameters are Å in part (a), 14 Å in part (b) and 17 Å in part (c).

The nature of the band gap for –H terminated nanowires appears to show some dependence on the diameter. From GGA-PBE, we see that the smallest diameter H-terminated nanowire has a direct band gap, however, the smallest indirect gap is only 0.15 eV larger, and as the nanowire diameter increases, the band gap changes to an indirect gap, similar to bulk Ge.

Examining the band structures of –NH₂ and –OH terminated GeNWs, we see that these surface terminations also show the quantum confinement effect, with a band gap reduction of 0.8 eV for the –OH terminated nanowires and 1 eV for the –NH₂ terminated nanowires on going from the smallest to the largest diameter nanowire. We note that the magnitude of the...
Figure 7.16: One-dimensional GGA-PBE band structure for (100)-oriented Germanium nanowires with -OH termination. The Germanium nanowire diameters are 10 Å in part (a), 14 Å in part (b) and 17 Å in part (c).

The band gap change as the nanowire diameter increases is smallest for the –OH terminated nanowires and largest for the –H terminated nanowires.

In terms of the nature of the band gap, we find an indirect band gap for 10 Å nanowires terminated with NH$_2$ (the smallest indirect gap is 0.2 eV larger) and a direct band gap for the 14 Å and 17 Å nanowires, with a direct band gap also found for all –OH terminated nanowires. Thus, not only magnitude, but also the nature of the band gap can be modified by chemistry that changes the surface termination of the nanowire. This will be explained using PDOS in pages 164 and 165.
We now compare the effect of the surface termination on the band gap of nanowires of a fixed diameter. Figure 7.17 (a) plots the band gap against nanowire diameter for the –H, -OH and -NH₂ terminating groups from GGA-PBE and figure 7.17 (b) shows the band gap against nanowire diameter for 10 Å nanowires with the three surface terminations from HSE06, comparing with the GGA-PBE values. Figure 7.18 shows the band structure for the 10 Å diameter nanowire with the –H, -OH and –NH₂ surface terminations from HSE06 to compare with the GGA-PBE results.

The first observation is that for a given nanowire diameter, the –OH surface termination strongly reduces the magnitude of the band gap, with a reduction of 1.1 eV over the -H terminated 10 Å diameter nanowire. While the magnitude of this difference reduces as the nanowire diameter increases, it still persists for the 17 Å diameter nanowire and this surface termination always reduces the band gap compared to –H termination. We attribute the fall off in the magnitude of the band gap reduction with increased nanowire diameter to the surface to volume ratio in the nanowires – the smallest diameter nanowire has the largest surface to volume ratio and the interaction of the surface Ge atoms with oxygen will show the largest perturbation of the band edges and thus the largest change to the band gap. As the wire diameter increases the surface to volume ratio decreases and the effect of the Ge-O bonding reduces so that the change to the band gap is smaller.
Table: 7.3 the magnitude and nature (direct or indirect) of the band gap of (100) oriented Ge nanowires for different wire diameter and different terminal groups.

<table>
<thead>
<tr>
<th>Diameter of GeNW (Å)</th>
<th>Eg (eV) GGA-DFT</th>
<th>Eg (eV) Hybrid-DFT</th>
<th>Type of band gaps</th>
<th>Mobility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (-H)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.7</td>
<td>3.2 (Indirect)</td>
<td>Direct</td>
<td>High</td>
</tr>
<tr>
<td>14</td>
<td>1.7</td>
<td></td>
<td>Indirect</td>
<td>Low</td>
</tr>
<tr>
<td>17</td>
<td>1.1</td>
<td></td>
<td>Indirect</td>
<td>Low</td>
</tr>
<tr>
<td>Amino (-NH₂)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.8</td>
<td>2.45 (Indirect)</td>
<td>Indirect</td>
<td>High</td>
</tr>
<tr>
<td>14</td>
<td>1.3</td>
<td></td>
<td>Direct</td>
<td>Low</td>
</tr>
<tr>
<td>17</td>
<td>0.8</td>
<td></td>
<td>Direct</td>
<td>Low</td>
</tr>
<tr>
<td>Hydroxyl (-OH)</td>
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<td>14</td>
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<tr>
<td>17</td>
<td>0.7</td>
<td></td>
<td>Direct</td>
<td>Low</td>
</tr>
</tbody>
</table>

The –NH₂ terminating group reduces the band gap by 0.8 eV for the 10 Å diameter nanowire indicating that the effect of this surface termination is weaker than the –OH termination. Similarly to –OH termination, the difference between the band gaps for –NH₂ and –H terminated nanowires reduces as the nanowire diameter increases, with a similar origin in terms of surface to volume ratio as a function of nanowire diameter. These results do show clearly that the band gap of Ge nanowires can be modified over a wide range (up to 1.1 eV) by suitable surface termination chemistry.
Figure 7.17: Computed band gap as a function of the diameter for (100) oriented Germanium nanowires for the surface terminations studied in this thesis. (a) GGA-PBE results. (b) GGA-PBE and HSE06 results for 10 Å diameter nanowires.

Lastly, we compare the HSE06 calculation of the band gaps for the different terminal groups in 10 Å diameter Ge nanowires to the GGA-PBE band gaps. While the GGA-PBE band gaps are clearly underestimated compared to hybrid DFT, figure 7.17 (b), the change in the band gap when –H is substituted for –OH or –NH₂ is the same, with a significant change of 1 eV in the magnitude of the band gap with –OH termination from both DFT approaches. The nature of the band gap for the –OH and –NH₂ terminated nanowire is also unchanged when comparing GGA-PBE and HSE06. Thus, given that hybrid DFT generally provides accurate band gaps for semiconductors, we can be confident that for determining trends in band gap modification of Ge nanowires with different surface terminating groups and wire diameter, GGA-PBE would be entirely suitable.
Figure 7.18: One-dimensional band structure for 10 Å diameter Germanium wires along (100) with different surface terminations (a) –H (b) –NH$_2$ and (c) –OH. Result from hybrid DFT (HSE06) calculation.

To understand in more detail the effect of the surface terminating group on the band gap of Ge nanowires we examine the electronic density of states projected (PDOS) onto the Ge 4p, H 1s, O 2p and N 2p electronic states. The PDOS plot for the Ge nanowires with -H, -NH$_2$ and -OH termination are shown in figure 7.19 (a), (c) and (d) for 10, 14 and 17 Å diameter nanowires. The PDOS shows that the valance and conduction band edges of H-terminated Ge nanowires are derived from Ge states, with no significant contribution of the H 1s states to either the valence or conduction bands.
Figure 7.19: Projected electrons density of states (PDOS) for (a) 10 Å (from GGA-PBE), (b) 10 Å (from HSE06), (c) 14 Å (from GGA-PBE) and (d) 17 Å (from GGA-PBE) diameter Ge (100) nanowires, with different surface terminations (–H, –OH, –NH₂) decomposed into orbital contributions of Ge 4p, H 1s, O 2p, and N 2p as indicated. Energies are referenced with respect to the conduction band edge.

For the –OH and –NH₂ surface terminations the valence band edge is shifted upwards with the largest shift being found for the –OH termination. This results in the reduction of the valence-conduction band energy gap with the largest reduction for –OH termination and the band gap for –NH₂ termination lying between the band gaps of the –OH and –H terminated nanowires. We also observe that in the VB region, the offset of the highest energy O 2p and N 2p states from the Ge 4p states decreases as the nanowire diameter increases, which is...
consistent with the smaller change in the band gap with these surface terminations compared to –H termination as the diameter of the nanowire increases.

Comparing the PDOS from GGA-PBE with HSE06 for the 10 Å diameter nanowires, figure 7.19 (a) and figure 7.19 (b), we see that the same upwards shift of the valence band edge is found from both DFT approaches, giving further confidence in using GGA-PBE to examine the changes in the band gap of semiconductor nanowires with surface modification.

We have investigated the mobility of different diameters and surface terminations of germanium nanowires. By looking the graph of dispersion relation of E vs K we can roughly estimated the mobility of Ge nanowires. Table 7.3 shows the mobility of different diameters and surface terminating group of Ge nanowires. As we can see table 7.3 the small diameter of different terminating group of Ge nanowires are higher mobility than the big diameter nanowires.

7.2.4 Optical properties of different terminal group of GeNWs

Figure 20 (a) – (c) shows the computed absorption coefficient plotted against energy for the –H, -NH₂ and -OH surface terminating groups for the 10, 14 and 17 Å Ge nanowires. In figure 7.21 also shows the absorption coefficient versus energy for different diameter nanowires with a given surface termination. These plots show that the position of the absorption edge shifts to lower energy as the surface terminating group changes from –H to –NH₂ to –OH, consistent with the change in the band gap for these surface terminations. We find this result at all nanowire diameters and we also see that the shift in the absorption edge with –OH and –NH₂ termination is smaller for the largest diameter nanowire compared to the smallest diameter nanowire, which is also consistent with the results for the computed band gaps.
Thus, the surface environment has a significant role in determining the optical properties of the nanowires.

Figure 7.20: Calculated absorption coefficient plotted against energy for (100)-oriented Ge nanowires from GGA-PBE. (a) 10 Å diameter with the three surface terminating groups, (b) 14 Å diameter and (c) 17 Å diameter.
Figure 7.21 Absorption coefficient of different diameter of (100)-oriented Germanium nanowires. (a) -H, (b) -NH$_2$, and OH terminal GeNW. Result from DFT calculations within GGA-PBE.

### 7.2.5 Conclusions

In summary, we have successfully generated different amorphous layer thicknesses of the a-Si/c-Si and a-Si:H/c-Si nanowires from heat and quench. We perform the 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. The DOS of the core-shell nanowire has no band gap, with a finite DOS around the Fermi level. The unrelaxed structure shows a significant density of states in the gap region. With DFT relaxation and addition of hydrogen we have achieved
a significant reduction in the DOS in the gap regions. Even if the hydrogenated NW has a finite density of states, this could also arise from the presence of undercoordinated Si atoms in the NW surface, but this is an interesting area for further exploration. The optical gap of the a-Si/c-Si and a-Si:H/c-Si NWs are larger than bulk a-Si:H. The main reason for this is due to quantum confinement effect. This gives a band gap increase compared to bulk as the wire diameter decrease.

We have also shown from DFT calculations that the diameter of Ge nanowires and the nature of surface terminating groups play a significant role in both the magnitude and the nature of the nanowire band gaps. For a given surface termination (-H, -NH₂ or -OH) the band gap decreases for larger diameter nanowires, while for a given nanowire diameter, terminating with -OH can reduce the band gap by up to 1.1 eV. This surface terminating effect weakens for larger diameter nanowires as a result of the smaller surface to volume ratio. The density of states shows the presence of N 2p and O 2p states above the original VB edge of the Ge nanowire which is the origin of the band gap reduction with these surface terminating groups. We have also shown how the 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.
CHAPTER 8

8 Conclusions and further work

8.1 Conclusion

Classical molecular dynamics and first principles DFT calculations have been performed to generate structural models of 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). Significant oversaturation leads to formation of nano c-Si regions in an a-Si matrix (maroudas)\textsuperscript{78-80}. At the same time, mid-gap states associated with dangling Si and strained Si-Si bonds disappear at saturation but reappear at mild oversaturation, consistent with the evolution of the optical gap.

Standard structural analyses (RDF, tetrahedral angles) of our models are unable to provide a detailed description of the influence of H content. However, the distribution of Si-Si bond distances provides the key to these changes 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 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.

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.

Analysis of the RDF indicates a structural interface region one layer thick in both a-Si/c-Si and a-Si:H/c-Si interfaces. However, the electronic density of states shows new electronic states forming as a result of disorder, even in the seemingly crystalline layers, indicating that an electronic interface is formed between a-Si (and a-Si:H) and c-Si that is larger than the structural interface. The 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 shows optical band gaps that are around 1.25 eV, independent of the precise thickness of the 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 and a-Si:H/c-Si interface defects on the offsets and implications for device performance. The band offsets at the interface have a substantial influence on the solar cell characteristics and lead to several consequences for charge-carrier transport and
recombination in heterojunction devices. The band offsets depend on the amorphous layer thickness and increase with thickness and the valence band offset of the highest layer thickness of (100), (110) and (111) orientations is converged to 0.65 eV. This value is consistence with the highest valance band offset value reported in the literature. By controlling the amorphous layer thickness we can potentially optimise the solar cell parameters. We investigated the effect of surface orientation on interface defect states. In our study we find that the amount of dangling silicon formation along the interface region depends on the surface orientation. (100) and (111) surface orientations create the least and the most dangling silicon in the interface region, respectively. But the effect of orientation on the band offsets for the same a-Si:H thickness is not significant.

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 and performed 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. The DOS of the core-shell nanowire has no band gap, with a finite DOS around the Fermi level. The unrelaxed structure shows a significant density of states in the gap region. With DFT relaxation and addition of hydrogen we have achieved a significant reduction in the DOS in the gap regions. Even if the hydrogenated NW has a finite density of states, this could also arise from the presence of undercoordinated Si atoms in the NW surface, but this is an interesting area for further exploration. The optical gap of the a-Si/c-Si and a-Si:H/c-Si NWs are larger than bulk a-Si:H. The main reason for this is due to quantum confinement which gives a band gap increase compared to bulk as the wire diameter decreases.

The core-shell structures with large a-Si regions increase the distortion in the peak of the Si-Si distances at around 2.34 Å and the number of strained Si bonds, with Si-Si distances > 2.4
Å, increases. When we compare the Si-Si strained bonds of a-Si nanowires with bulk a-Si, the nanowire has less strained bonds than bulk a-Si. This has a potential advantage to reduce the presence of gap states as well as the band tails which are partially contributed from the strained Si-Si bonds.

We examine three different surface terminating chemical groups, -H, -OH and –NH$_2$ in (001) GeNW and show how the diameter and surface termination determine the magnitude and nature of the nanowire band gap and the absorption spectrum of the nanowires. 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.

In general, all our findings related to bulk a-Si, interfaces of a-Si/c-Si, a-Si/c-Si core-shell nanowires and Ge nanowire have lead to new enhancements in our understanding of these important materials and give a bench mark for further research and very useful information for experimental researchers and amorphous silicon manufacturers in order to improve the solar cell performance. In literature one can find conflicting reports on the role of hydrogen in amorphous silicon. Our model allows us to address the solution for those conflicts. One aspect that will need further work is in a-Si/c-Si NWs. With the necessity to study large diameter silicon nanowires, we were able to address initial results regarding different layer thickness of a-Si in a-Si/c-Si core-shell nanowires of a given diameter but these initial results are interesting enough to warrant further exploration.
8.2 Further work

We have studied and addressed key issues related to H content in amorphous silicon, a-Si/c-Si interfaces and the effect of orientation and different layer thickness layer on electronic and optical properties, band offsets and interface defect states, as well as structural characterization of core-shell nanowires, and we have presented a comprehensive study of this well-known fascinating material. But still further work is needed to address a complete understanding of our model materials. There are some interesting further aspects that can be explored based on this thesis.

- A detailed study of electronic, optical and charge transport properties of a-Si/c-Si and a-Si:H/c-Si core-shell nanowires.
- Important issues to study can include doping, point defects (at interface and bulk), and surface terminations.
- Finally parameters from these structures such as optical gaps can be used in finite element modelling of large scale structures as part of materials parameters sets.

In this thesis we address the solution of issues related to bulk a-Si:H, the interface between a-Si:H/c-Si a-Si/c-Si core-shell nanowires and Germanium nanowires. All our findings related to bulk a-Si, interfaces of a-Si/c-Si, a-Si/c-Si core-shell nanowires and Ge nanowire have lead to new enhancements in our understanding of these important materials and give a benchmark for further research and very useful information for experimental researchers and amorphous silicon manufacturers in order to improve the solar cell performance.
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