Atomistic Models of Amorphous Semiconductors

Proefschrift

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Chapter 1

Introduction

Matter that we encounter in our daily lives comes in different forms. The usual division is based on the phase of the system: solid, liquid or gaseous. Solids are rigid, liquids flow and gases can be compressed. Apart from these mechanical properties we can come up with several other criteria on how to categorize matter. These can be based on how the materials interact with light, conduct electricity, respond to a magnetic field or on their chemical composition. Yet another approach could be to sort matter by the degree of ordering.

Crystals are the most ordered forms of matter. They are composed of unit cells repeated periodically in all three dimensions. The order is preserved over macroscopic distances. For naturally occurring minerals it is often possible to deduce the crystal structure just by examining its facets. Quite surprisingly we can predict the major properties of a silicon wafer, containing $\sim 10^{23}$ atoms, just by considering the unit cell containing only two atoms!\(^1\) The existence of translational symmetry allows us to study a wide range of solids and lies at the heart of solid state physics. In real life situations crystals contain various imperfections. These include point defects (e.g. vacancies and interstitial atoms) and line defects (e.g. dislocations) that interrupt the perfect ordering. Although there is no practical limit to the size of the crystals (lengths of 11 m were reported),\(^2\) polycrystalline materials are far more common. A common example are metals that consists of grains. Grain boundaries impede the movement of dislocations and make the material more hard and brittle.

For two centuries long-range order was closely associated with periodicity. It turns out that there exist structures that are ordered at long
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Figure 1.1: Penrose tiles consisting of two types of rhombi.

Figure 1.2: The structure of liquid crystals. From left to right: crystal, smectic LC, nematic LC and liquid.

range but are not periodic - the so-called quasicrystals. Their discovery has changed the way we think about long-range order and augmented the definition of the crystal. Nowadays crystals are defined as structures that produce essentially a discrete diffraction pattern when exposed to radiation. An example of a quasicrystal in two dimensions are the Penrose tiles depicted in Fig. 1.1. They consist of fat and skinny rhombi completely filling the plane. Note the 5-fold rotational symmetry, normally forbidden in periodic crystals.

Many organic compounds form an intermediate phase during the liquid to solid transition (see Fig. 1.2). This phase possesses order of crystals but can flow as a liquid at the same time. It is known under the term liquid crystals (LCs). The building blocks are molecules in the shapes of rods or discs that interact through relatively weak Van der Waals forces. In nematic LCs the molecules are positioned randomly in space, but they are oriented in the same direction (flow is possible along the direction of
their orientation). Smectic LCs are composed of layers that slide over each other. Finally the orientation of molecules in cholesteric LCs follows a helical path. They have found a widespread use in display technology.

The forms of condensed matter described above are composed of atoms (molecules) ordered at long range. A large group of materials, however, does not fall into this category. The terms non-crystalline, disordered, amorphous, vitreous or glass are used. The terminology varies between authors, leading to some confusion. The first three terms are rather general, while the last two are mostly used to describe solids prepared by cooling from a liquid. Although amorphous materials are at the bottom part of our “order hierarchy”, the view that the atoms are placed randomly in space is not correct. The chemical bonding assures order at the distance of several bond lengths, the so called short-range order. The ordering over longer length scales is, however, lost. In the past, it was suggested that amorphous solids are in fact liquids with a very high viscosity. A popular myth connected to this idea states that glass windows in cathedrals are thicker at the bottom. In reality the time scales over which flow could be observed is well beyond the age of the Universe. The non-uniform thickness of the ancient windows is caused by the production technique.

An ubiquitous example of an amorphous solid, already mentioned above, is glass. In common speech this refers to the soda-lime glass, used to make windows and containers. The composition is rather complex, containing \( \sim 75\% \) of SiO\(_2\) (silica), Na\(_2\)O (soda) and CaO (the lime component). Soda is added to lower the processing temperature from 2300 °C of pure silica to 1500 °C. Silica based glasses occur in nature, for example obsidian is formed by a rapidly cooled lava. It has a black color due to the many impurities. Apart from silica based glasses there are other types such as: borate (B\(_2\)O\(_3\)) or phosphate (P\(_2\)O\(_5\)) glasses. Although the structure and coordination can differ a common feature is their optical transparency. This implies that there is a range of forbidden energies, a band gap. Visible photons, with energies from 1.7 to 3.2 eV, cannot excite electrons across this gap and pass through the glass. The formation of a band gap is, however normally associated with crystalline semiconductors or insulators. A theoretical understanding of the electronic structure of glasses, came much later than that of the crystals. Sir Nevill Mott, who made a considerable contribution to these theories, comments on this in his 1977 Nobel lecture:

“... it is curious, therefore, that no one much earlier than my coworkers and I in Cambridge less than ten years ago seems to
Another example of amorphous solids are metallic glasses. These non-transparent glasses do not occur naturally and are usually fabricated as either alloys of two or more metals (e.g. Fe-Zr, Zr-Be-Ti-Cu-Ni) or as a compound of a metal and a metalloid (P, Si, Ge, B). In fact the first metallic glass, prepared in 1960 was of this type. It was an Au$_{75}$Si$_{25}$ alloy prepared by melt spinning. This method produces thin ribbons by applying the melt onto a spinning wheel. Fast cooling rates of the order of $10^6$ K/s can be achieved. The coordination in metallic glasses is close to 12, although the density is lower than in their crystalline counterparts. The macroscopic properties of metallic glasses stem directly from their disordered structure. Conductivity decreases by 2-3 orders of magnitude. Introducing disorder leads to a lower Curie temperature in magnetic alloys. An increased resistivity leads to smaller eddy currents and possibly to more efficient transformers. Unlike the crystalline counterparts, they do not contain imperfections such as dislocations or grain boundaries. This leads to an increased strength, and a higher resistance to wear and corrosion.

Both insulating and metallic glasses described above are prepared by cooling from melt. This process is depicted in Fig. 1.3. Cooling a liquid results either in crystallization or in formation of a glass. During crystallization there is an abrupt change in the volume, occurring at the melting temperature $T_m$. Atoms rearrange into energetically more favorable positions and form a crystal. Most of the time this is associated with a decrease in volume. Exceptions are materials that form solids with an open struc-
ture such as silicon or water. Crystallization, can however be bypassed, when the concentration of nucleation sites is low (high purity) and the crystal growth is slow (high viscosity of the liquid). Enthalpy then decreases continuously below $T_m$. Lowering the temperature further, below the glass transition temperature $T_g$, results in the formation of a glass. $T_g$ is defined by the position of the kink on the cooling curve. Another definition is based on a threshold viscosity of $10^{12}$ Pa s. For comparison, the viscosity of peanut butter at room temperature is $250$ Pa s. Note that the formation of a glass is not a true thermodynamical phase transition, but a kinetic phenomenon. $T_g$ depends on the thermal history of the system and on the cooling rate. In principle any material can be prepared as glass. Some materials form glasses easily. Oxide glasses, for example, require cooling rates of only $10^{-4}$ K/s. Pure metals, however, require extremely fast cooling rates of $10^{12}$ K/s. For metal alloys the critical cooling rate is lower. A multi-component alloy, such as the one mentioned previously, can be prepared with rates close to 1 K/s. The large number of elements leads to complicated unit cells, and hence the atoms do not have the time to rearrange to form a crystal. Additionally the elements have different atomic radii, what leads to a small free volume and consequently to a large viscosity. Amorphous solids can be also prepared by other methods. Thin films are prepared by deposition from the gas phase. Sputtering, for example, is a physical vapor deposition technique, during which material is ejected from the target and subsequently condenses on the substrate. During chemical vapor deposition, molecules of the precursor gas chemically bind to the substrate. The chemical reactions are initiated by igniting a plasma or by decomposing the gas thermally. Application of pressure can lead to amorphization too, as was demonstrated for ice. Other techniques include irradiation of crystals and mechanical milling. The division between glasses and other amorphous solids is probably artificial. It is very well possible that materials with the same structure can be prepared by different techniques.

The structure of liquids and amorphous solids is quite similar. There is short range order at several inter-atomic distances but the long-range order is lost. The main difference is of course that amorphous materials are rigid and liquids flow. Hence on the microscopic level atoms in solids just vibrate around their equilibrium position. In liquids time plays a more important role and various time dependent correlations functions can be defined.
When considering order, gasses can be considered as the antipode of the crystal. The ideal gas consists of non-interacting point particles. There is no average bond length or even a minimum pair separation. The system is completely disordered.

1.1 Amorphous semiconductors

Studies on amorphous semiconductors are motivated by the lack of satisfactory understanding of their properties, especially the ones that are different from the crystals. A large part of research is motivated by applications that are in use today or by promising future applications. Amorphous semiconductors are usually divided into two groups: chalcogenide and tetrahedrally bonded semiconductors.\(^7\)

Chalcogenide semiconductors are based on the group 16 elements: S, Se and Te. They are either elemental or form compounds with the group 15 elements (P, As, Sb) and group 14 elements (Si, Ge, Sn). The structure of chalcogenides is more complex than that of tetrahedrally bonded a-Si or a-Ge. Often they consist of chain- or layer-like structures leading to ordering at medium range. The bonding within the chains is covalent, while the bonding in-between is much weaker (Van der Waals bonds). In general, chalcogenide semiconductors are good glass formers and can be prepared by both cooling from liquid and vapor deposition. The best studied chalcogenides are a-Se, As\(_2\)Se\(_3\), GeSe\(_2\). In the last two compounds selenium can also be exchanged by sulfur.

The most successful application of chalcogenides is the photocopier, introduced by Xerox. A key component of the machine is a drum coated with amorphous selenium. The copying process starts with charging the drum. At dark the selenium behaves like an insulator and retains the charge. Next the original document is illuminated with light that reflects from the white space onto the drum. Since a-Se is photo-conductive the surface charge on the exposed areas recombines. Dark areas, such as letters, do not reflect light and hence the charge remains on the a-Se film. Finally, the copy is made by applying positively charged toner particles on the drum and than on paper.

Another widely used application are rewritable optical discs (CDs, DVDs) based on Ge\(_2\)Sb\(_2\)Te\(_5\).\(^8\) The binary data is encoded as sections with

\(^{*}\)We will use the new group numbering, recommended by the International Union of Pure and Applied Chemistry.
low and high reflectivity that correspond to the amorphous and crystalline phase of the material respectively. At first the chalcogenide is in its crystalline phase. During writing a relatively intense laser beam is used to heat the material above the melting temperature. After the laser moves away the chalcogenide cools rapidly and forms a glass. Using a lower intensity laser one can heat the amorphous section above the glass transition temperature. This leads to crystallization and the “amorphous bit” is erased. Reading is performed with the very same laser set at minimum intensity.

Chalcogenide semiconductors are generally transparent in the infrared region. Thus other applications include lenses, windows and fibers in various optical devices that operate in the infrared range, e.g. night vision and thermal imaging.

Tetrahedrally bonded semiconductors constitute the second group of amorphous semiconductors. Prominent examples are silicon and germanium. These are group 14 elements that form covalently bonded solids with an open structure. Carbon has an amorphous phase too. It is, however, considered to be an insulator because of its large band gap. In their pure form a-Si or a-Ge are prepared by sputtering or thermal evaporation. Various types of chemical vapor deposition (CVD) produce films that contain hydrogen and are therefore denoted as a-Si:H or a-Ge:H. Adding methane (CH$_4$) or ammonia (NH$_3$) to the source gas allows to produce silicon carbide (a-SiC$_x$:H) or silicon nitride (a-SiN$_x$:H) respectively. The composition of these alloys can be changed continuously, which allows to tune the band gap in a wide range of energies.

Our understanding of the structure of tetrahedrally bonded semiconductors is largely influenced by the work of W.H. Zachariasen on oxide glasses. Already in 1932 he realized that the gross properties of oxides in the crystalline and amorphous phases are similar. He concluded that the bonding and structure at short distances has to be the same. On the other hand, Zachariasen was aware of the lack of long range order in glasses. He proposed that the glass is formed by a network that preserves the coordination of atoms, but lacks long-range periodicity. Nowadays we refer to this concept as the continuous random network model. Thus a-Si, for example, is formed by tetrahedral units, where most of the atoms have 4 bonds and the average bond angle is 109.5°. The situation is similar in hydrogenated silicon (see Fig. 1.4), where H forms only one bond. The number of bonds can be calculated as 8 minus the number of valence electrons of the particular element (8-N rule). This rule was proposed by Mott
to explain the difficulty of doping a-Ge.\textsuperscript{10} Thanks to a greater flexibility of the amorphous network a dopant such as phosphorus will assume its normal 5-fold coordination. Thus electrons are not donated to the conduction band but are used up for bonding. One often thinks of the amorphous network as being homogeneous. It seems, however, that the reality is more complex than that. Analysis of infrared absorption suggests that a-Si:H contains vacancies (di-vacancies and larger) with surfaces passivated by hydrogen.\textsuperscript{11,12} Transmission electron microscopy was used in a local mode to study nanometric volumes of amorphous silicon. Scanning across the film resulted in large fluctuation in the measured intensity, indicating medium-range order. The authors concluded that a-Si:H actually consists of nanometer-size crystallites embedded in an amorphous matrix.\textsuperscript{13}

A theoretical description of the electronic structure of amorphous semiconductors came much later than that of their crystalline counterparts. In principle, concepts such as the Bloch theorem, the Brillouin zone and the concept of a band structure cannot be applied, because of the lack of periodicity. The formation of band gaps was also commonly attributed to periodicity. Already in 1931, Kronig and Penney showed that the range of energies of an electron, in a periodic rectangular potential, contains forbidden intervals.\textsuperscript{14} The existence of band gaps in amorphous solids was demonstrated many years later. In 1971 Weaire showed, that preserva-
tion of tetrahedral bonding between nearest neighbors leads to band gap formation. In Figure 1.5 we illustrate the features of the electronic structure of an amorphous semiconductor on a-Si:H. There are three types of states. The first type are extended states (in black and gray color), which are delocalized and similar to states in the crystals. In experiments, it is common to assume that the DOS of extended states, near the band gap (in gray), changes as the square root of energy. The second type are tail states (in red color) that originate from the disorder and are not present in crystals. Their DOS has an exponential dependence on energy and are separated from the extended states by the so-called mobility edge. In Figure 1.5 the valence and conduction mobility edges are located at 0 and 1.7 eV respectively, giving a mobility gap of 1.7 eV. Values found in literature vary. R.A. Street, for example, reports a value of 1.85 eV. The discrepancies might be caused by differences in the studied material and/or by the interpretation of experimental data. In the case of optical measurements, one has to assume a certain functional form of the DOS. At present, several such forms are in use. Note that the mobility gap of a-Si:H lies in between the indirect band gap (1.1 eV) and the direct band gap (3.4 eV) of crystalline silicon. The third type of states originate from defects (in green color). A device quality a-Si:H contains about 10^{16} cm^{-3} defects.

Hydrogenated amorphous silicon and its alloys have applications in large area electronic devices such as solar cells and displays. A photovoltaic technology that should have a noticeable share in the global electricity generation has to be based on abundant materials. Right after oxygen, silicon is the second most abundant element in Earth’s crust. The amorphous form of silicon has several advantages over c-Si that currently dominates the PV market. Because of the “direct” nature of its band gap it absorbs visible light more strongly. Thus a-Si:H solar cells can be much thinner (~300 nm) than crystalline ones (~250 μm). Thin-film solar cells are lightweight and mechanically flexible. Another advantage is that a-Si:H can be deposited cheaply and over large areas with the CVD method. Crystalline PV modules are assembled from smaller wafers. Ingots of c-Si are crystallized from a melt, purified and than sawed into wafers, what obviously requires more energy and is more costly. As of 2010 the average module efficiency of commercially available a-Si:H based cells is 8 %. Crystalline modules reach higher efficiencies of 18 %. One has to realize, however, that a more important parameter than the efficiency is the cost of the
Figure 1.5: Density of states in a-Si:H on a linear (top panel) and logarithmic (bottom panel) scale. The insets show a detail of the valence mobility edge. The plot is a combination of our calculated results on a Si$_{216}$H$_{27}$ model (black line) and the empirical model by O’Leary.\textsuperscript{16}
1.2. **BACKGROUND AND GOALS OF THE THESIS**

Figure 1.6: A standard a-Si:H solar cell (not to scale).

Produced electricity and here the thin films have a potential advantage.

Apart from solar cells, which are essentially diodes, thin film transistors (TFTs) are also fabricated. The channel is mostly made of a-Si:H and the dielectric of a-SiN:H. A rather ubiquitous application of TFTs is in the liquid crystal display industry.\(^{22}\)

### 1.2 Background and goals of the thesis

As we discussed in the previous section, the efficiency of silicon thin-film solar cells is lower than the efficiency of c-Si cells. Naturally, there is an ongoing effort to improve this situation. A standard a-Si:H solar cell consists of an intrinsic absorber layer sandwiched between p- and n-doped layers (see Fig. 1.6). A photon absorbed in the intrinsic part creates an electron–hole pair. The charge carriers flow towards the electrodes because of an internal electric field due to the doped layers. The solar cell can then be connected to an external load to perform useful work.

An interesting question arises, related to the efficiency of the solar energy to electricity conversion. Applying the laws of thermodynamics to an idealized solar cell, with a single absorber layer, one arrives at a maximum efficiency of 32.5%.\(^{23}\) This value is relatively low, because the solar spectrum is not utilized effectively. Photons with lower energy than the absorber band gap are not absorbed and pass through the cell. High energy photons are absorbed and excite electrons high in the conduction band. The surplus energy of the electrons is, however, quickly converted into heat and thus lost. One can get around this problem by stacking several solar cells on top of each other. Each of the solar cells will absorb light in a different energy range. This is the concept of a multi-junction solar cell depicted schematically in Fig. 1.7. In this particular case the
A triple-junction solar cell. The light is entering from the top. Right: The SELECT absorber consisting of quantum dots and a multilayer.

device consists of three cells. The band gap of absorber layers decreases from top to bottom. The material with the highest band gap is on the top (in blue), so that the low-energy light can pass through it. The maximum efficiency of an ideal triple-junction device has a considerably higher value of 49.7\%.

In order for the multi-junction concept to work, a range of materials with suitable band gaps is necessary. Nanotechnology offers methods to achieve this variety with a single material. When the dimensions of a semiconductor are reduced to the nanometer scale, the band gap can be tuned due to quantum confinement effects. The nanostructures can have different dimensions: 0 (quantum dots), 1 (wires) or 2 (multilayers). A proof of concept of the above described approach was investigated in the project Silicon-based superlattices with spectrum-selective absorbers or SELECT for short. The SELECT absorber is schematically depicted in Fig. 1.7. It contains quantum dots, made of lead and cadmium chalcogenides that are strong and spectrum-selective absorbers. The extraction of charge carriers is facilitated by a multilayer with an effective band gap tuned to the band gap of the quantum dots.

In this thesis we investigate a multilayer structure that consists of alternating layers of a small (a-Si:H) and a large (a-SiN:H) band gap material. The main goal is to provide a better understanding of the electronic structure of the multilayer. In particular we are interested in the valence and
1.2. BACKGROUND AND GOALS OF THE THESIS

Conduction band offsets between the two materials, since the offsets will to a large extent determine the charge carrier transport through the structure. Theoretical calculations of band offsets were successfully applied to a wide range of crystalline semiconductors. A direct application of these methods to amorphous semiconductors can, however, prove difficult. This is because amorphous semiconductors do not have a sharp band edge as was illustrated for a-Si:H in Fig. 1.5. It is thus important to find a method that would distinguish between the different types of states (extended, tail and defect) and locate the mobility edge.

First amorphous multilayers were fabricated by Abeles and Tiedje. Results of optical and electrical measurements on these structure are often explained solely in terms of confinement effects of charge carriers. Other authors, however, claim that these effects are largely overestimated. Systematic errors in determination of optical band gaps and a transition between transport mechanisms are offered as alternative explanations. A goal closely related to the calculation of band offsets is to evaluate the magnitude of quantum confinement in the a-Si:H/a-SiN:H multilayer.

The investigation of the electronic structure has to be build on reliable structural models. In other words, the generated theoretical models need to have a realistic short range order. A related objective is to characterize the short range order in terms of pair-distribution functions and structure factors. The quality of the models will be checked against diffraction experiments (where available).
Chapter 2

Methods

In this chapter we introduce several theoretical results that are used throughout the thesis. In the first section we apply the theory of scattering to disordered solids. This will allow us to compare the structure of theoretical models with experiment. All of the calculations presented in this thesis were performed with the Vienna *ab-initio* simulation package (VASP).\textsuperscript{40–42} This program is based on density functional theory that is described in the second section.

2.1 Structure of disordered solids

Knowledge of the structure on atomic scale is often necessary to understand the properties of condensed matter. The structure can be probed by exposing matter to a flux of particles. X-rays interacting with the electrons and neutrons interacting with the nuclei are often used for this purpose. A common feature is that both particles are described as waves with wavelengths comparable to the inter-particle distance. This causes interference effects that encode the structural information into the scattered radiation. The application of x-rays to structure determination resulted in as many as nine Nobel prizes, awarded mostly in chemistry. Neutrons are used less often, since their generation is much more demanding. This is unfortunate, since they have several advantageous properties that are useful for structure determination. In the following we will derive an expression for the intensity of scattered neutrons.\textsuperscript{*}

\textsuperscript{*}A more detailed derivation can be found in the textbook of G.L. Squires.\textsuperscript{43}
A sample scattering experiment is schematically depicted in Fig. 2.1. During the scattering event the wave vector of the neutron changes from \( k \) to \( k' \). The difference between the initial and final wave vectors is known as the scattering vector \( q = k - k' \). The norm of the scattering vector is related to the scattering angle: \( q = 2k \sin \theta \). The area of the detector \( dS \) and its distance from the sample defines the solid angle \( d\Omega \), into which the neutrons are scattered. The quantity measured in the experiment is the so called differential cross-section \( \frac{d\sigma}{d\Omega} \). It is defined as the number of neutrons that are scattered per second into the solid angle and divided by the incoming neutron flux \( \phi \) and \( d\Omega \). Using Fermi’s golden rule to calculate the number of transitions from a single \( k \) state to a group of \( k' \) states we get:

\[
\frac{d\sigma}{d\Omega} = \frac{1}{\phi d\Omega} \frac{2\pi}{\hbar} \rho_{k'} |\langle k'|V|k \rangle|^2,
\]

(2.1)

where \( \rho_{k'} \) is the density of the final states and \( V \) denotes the interaction between the neutron and the sample. The neutrons are described by the following wave functions:

\[
|k\rangle = \frac{1}{\sqrt{Y}} e^{ik \cdot r} \tag{2.2}
\]

\[
|k'\rangle = \frac{1}{\sqrt{Y}} e^{ik' \cdot r} \tag{2.3}
\]

Here we imagine the system to be enclosed in a large box with volume \( Y \). To continue further we need to find expressions for the incoming neutron
flux $\Phi$ and $\rho_{k'}$. Flux is a product of the neutron density and velocity. For a single neutron in the box we get:

$$\phi = \frac{1}{Y} \frac{\hbar k}{m}. \quad (2.4)$$

We derive the expression for the density of final states in the following way:

$$\rho_{k'} = \frac{dN'}{dE'} = \frac{Y}{(2\pi)^3} \frac{k'^2 dk'd\Omega}{2m^2 \hbar^2 k' dk'} \quad (2.5)$$

$$= \frac{Ym}{(2\pi)^3 \hbar^2} k' d\Omega \quad (2.6)$$

The nominator was calculated by counting states in the reciprocal space. Only states that are periodic in the box are allowed. These lie on a regular grid in the reciprocal space, with a density of $Y/(2\pi)^3$. States scattered into the solid angle $d\Omega$ with energy $dE'$ lie in a cylinder with volume $k'^2 dk'd\Omega$.

The term in the denominator comes from a derivative of the kinetic energy. Substituting the expressions for $\phi$ and $\rho_{k'}$ into Eq. 2.1 gives:

$$\frac{d\sigma}{d\Omega} = \frac{k'}{k} \left( \frac{m}{2\pi h^2} \right)^2 Y^2 |\langle k'|V|k \rangle|^2. \quad (2.7)$$

Since we consider only elastic scattering the ratio of the wave vectors is equal to one. Next we turn to the derivation of the matrix elements. To describe the interaction between the neutron and the nuclei in the sample we will use the Fermi pseudo-potential:

$$V(r) = \frac{2\pi h^2}{m} \sum_j b_j \delta(r - r_j). \quad (2.8)$$

The Delta function is used because the nuclear interaction is short range ($10^{-15}$ m) compared to the neutron wave length ($10^{-10}$ m). The constants in front are chosen in such a way that for a single fixed nucleus we get a constant differential cross section (for all angles) equal to the square of the scattering length $b$. The matrix element can now be expressed in terms of the scattering vector as:

$$|\langle k'|V(r)|k \rangle| = \frac{1}{Y} \frac{2\pi h^2}{m} \sum_j b_j \exp(i \cdot r_j). \quad (2.9)$$
We finally arrive at an expression that relates the differential cross-section with the structure of the material:

\[
\frac{d\sigma}{d\Omega} = \left| \sum_j b_j \exp(i\mathbf{q} \cdot \mathbf{r}_j) \right|^2 \tag{2.10}
\]

\[
= \sum_i \sum_j b_i b_j \exp(i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)). \tag{2.11}
\]

Note that the volume of the box and other constants have canceled out.

So far we have assumed that all nuclei are identical. In reality the sample can contain different isotopes of a chemical element and even the same isotopes might be in a different spin state. For a macroscopic sample we safely assume the normal distribution for the \(b_i\) values and write:

\[
\bar{b}_i \bar{b}_j = \begin{cases} 
\bar{b}_i \bar{b}_j = \bar{b}^2 & i \neq j \\
\bar{b}_i \bar{b}_i = \bar{b}^2 & i = j.
\end{cases} \tag{2.12}
\]

The differential cross-section is usually separated into the coherent and incoherent part:

\[
\frac{d\sigma}{d\Omega} = N [b_{coh}^2 S(q) + b_{inc}^2], \tag{2.13}
\]

where \(b_{coh} \equiv \bar{b}\) and \(b_{inc} \equiv (\bar{b}^2 - \bar{b}^2)\). Both types of scattering lengths are known for most of the isotopes.\(^4\) The coherent term is the interesting one, while the incoherent term acts as a background, independent of the scattering vector. The structural information is fully contained in the so called static structure factor:

\[
S(q) = \frac{1}{N} \sum_i \sum_j \exp(i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)). \tag{2.14}
\]

The measured structure factor can be converted from the reciprocal space to the direct space by an inverse Fourier transform:

\[
g(r) - 1 = \frac{1}{\rho(2\pi)^3} \int_{S(q) - 1} \exp(-i\mathbf{q} \cdot \mathbf{r}) \, dq, \tag{2.15}
\]

where \(g(r)\) is the so called pair-distribution function.

For liquids and amorphous solids the scattering will be isotropic and the \(S\) and \(g\) functions simplify from 3 to one dimension:

\[
S(q) - 1 = \frac{4\pi \rho}{q} \int_0^\infty r (g(r) - 1) \sin(qr) \, dr \tag{2.16}
\]

\[
g(r) - 1 = \frac{1}{2\pi^2 \rho r} \int_0^\infty q (S(q) - 1) \sin(qr) \, dq. \tag{2.17}
\]
We can easily switch between the two representations depending on whether we are interested in short- or longer-range structure. In practice the structure factors are measured over a finite $q$ range. This can give artifacts in the measured pair-distributions. In Figure 2.2 we plot several pair-distributions of amorphous silicon measured with different maximum scattering vector. All authors used pure amorphous silicon with the exception of Bellissent et al., who’s material contained 16 at. % of hydrogen. It appears that measuring the structure factor over a smaller $q$ range gives an artificial broadening of the peaks in the pair-distribution.

In this section we have given expressions for the static structure factor and pair-distribution function. These functions allow us to check the structure of theoretical models against reality. Although we have considered only systems consisting of one element the formalism can be extended to compounds (see Sec. 3.5). It should be noted that although the one dimensional structure functions contain a lot of information, the structural information is not complete. In other words two different models can have the same pair-distribution. One has to go beyond two-body correlation functions to see the difference.
2.2 Density functional theory

Condensed matter physics and its sub-field solid state physics deal with systems that are composed of many atoms. This leads to a problem where a large number of particles (electrons and nuclei) interact with each other. The behavior of the particles is governed by the Schrödinger equation. Although its time independent form looks deceivingly simple $H\Phi = E\Phi$, it leads to a rather intractable problem. The Hamiltonian consists of kinetic and interaction terms for electrons and nuclei and a cross term due to electron-nuclei interaction. $\Phi$ is a complex function depending on all the position vectors of the electrons and nuclei and is defined in a $3 \times (N_{el} + N_{nuc})$ dimensional space. The situation was summed up by Dirac in 1929:

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these leads to equations that are too complex to be solved."

It is thus clear that we have to resort to some sort of approximations. The first thing one notices is that the nuclei are much heavier than electrons. For hydrogen the nucleus is 1863 times heavier than the electron. The ratio is increasing for the heavier atoms. One can argue that the motion of electrons is much faster and they view the nuclei as stationary. On the other hand the nuclei move relatively slowly and they experience only an average field from the electrons. This is the essence of the Born-Oppenheimer approximation. For electrons in a potential of fixed nuclei the Schrödinger equation reads:\footnote{We will use Hartree atomic units, where $m = e = \hbar = 1/(4\pi\varepsilon_0) = 1.$}

\begin{equation}
(\hat{T} + \hat{U} + \hat{V})\Psi = E\Psi \tag{2.18}
\end{equation}

\begin{equation}
\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_j \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|} \tag{2.19}
\end{equation}

There are two major ways to continue from here. The first possibility is to assume a certain form of the many-electron $\Psi$. This group of methods is often referred to as wave-function methods. Hartree suggested, to search for the wave function in the form of a product of single-particle wave functions: $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = \varphi_1(\mathbf{r}_1)...\varphi_N(\mathbf{r}_N)$. Applying the product to
2.2. DENSITY FUNCTIONAL THEORY

Eq. 2.19 leads to a set of equations that can be solved iteratively. Since the electrons are treated as independent the electron correlation due to the $1/|\mathbf{r}_i - \mathbf{r}_j|$ is not treated accurately. Electrons rather experience an effective electrostatic field that is calculated during the iterative procedure. Slater improved on this approach and arranged the single particle functions in a determinant. This assures that the resulting wave function is antisymmetric and that it satisfies the Pauli exclusion principle. Similarly, applying a single Slater determinant to Eq. 2.19 leads to a set of equations known as Hartree-Fock equations. Although the “exchange” is treated precisely the electron correlation is neglected. Several post Hartree-Fock methods with an improved description of electron correlation exist. The improved accuracy comes generally with an increased computational cost.

A second approach to the many-electron problem is based on the Density functional theory (DFT). As the name suggests the emphasis is on the electron density $n(\mathbf{r})$ rather than on the wave-function. Our desire to calculate the many-electron wave-function follows naturally from quantum mechanics: $\Psi$ contains all the information about the system and all observables of interest can be readily calculated as expectation values. This approach has also disadvantages. Since $\Psi$ is a function in a multi-dimensional space, the computational effort and the storage space increases as an exponential function of the system size. The approximate post Hartree-Fock methods scale more favorably as the 5–7th power of the system size. Nevertheless even with today’s computer power they are restricted to small molecules.

The first steps towards a rigorous formulation of DFT were taken by Hohenberg and Kohn in 1964. In their paper they consider the relation between ground state electron density $n(\mathbf{r})$ and the potential due to the positive nuclei $\mathbf{v}(\mathbf{r})$. It is rather straightforward that $\mathbf{v}(\mathbf{r})$, through the position of nuclei determines the Hamiltonian of the system and this in turn determines the ground state wave function and the density. What is not clear, whether the relationship $\mathbf{v} \rightarrow n$ can be inverted. The first Hohenberg-Kohn theorem states that this is indeed possible. The proof is rather simple and will be presented below. Suppose there are two systems, defined by the external potentials $\mathbf{v}$ and $\mathbf{v'}$ that differ by more than a constant. Each potential determines its own Hamiltonian, ground state
wave function, density and energy:

\[ v \rightarrow \hat{H}, \Psi, n, E \tag{2.20} \]
\[ v' \rightarrow \hat{H}', \Psi', n', E'. \]

From the variational principle it follows:

\[ \langle \Psi \mid \hat{H} \mid \Psi \rangle < \langle \Psi' \mid \hat{H} \mid \Psi' \rangle \tag{2.21} \]
\[ < \langle \Psi' \mid \hat{H} + \hat{V}' - \hat{V}' \mid \Psi' \rangle \]
\[ < \langle \Psi' \mid \hat{H}' \mid \Psi' \rangle + \langle \Psi' \mid \hat{V} - \hat{V}' \mid \Psi' \rangle \]
\[ E < E' + \int (v - v')n'(r)dr \]

In an analogous way we get:

\[ E' < E + \int (v' - v)n(r)dr \tag{2.22} \]

Adding the inequalities we arrive at:

\[ E + E' < E + E' + \int (v - v')(n'(r) - n(r))dr \tag{2.23} \]

It is clear that \( n(r) \) and \( n'(r) \) must be different. We have thus proved that the electron density determines the potential uniquely to within an additive constant.

The second Hohenberg-Kohn theorem is a restatement of the variational principle for the charge density. In quantum mechanics observables are calculated as expectation values from the wave function. For example the total energy can be calculated as

\[ E = \langle \Psi \mid \hat{T} + \hat{U} \mid \Psi \rangle + \langle \Psi \mid \hat{V} \mid \Psi \rangle. \tag{2.24} \]

Since the charge density is the new key variable we would need a prescription that would assign an observable value to a given charge density - a functional. For the total energy we can formally write:

\[ E[n] = F[n] + \int v(r)n(r)dr. \tag{2.25} \]

\( F[n] \) is a functional, often called universal because it is the same for all systems of interacting electrons. The second term is specific to the system
and, unlike the first one, we know how to write it explicitly. The second theorem states that for a given external potential, \( E[n] \) has a minimum that corresponds to the exact ground state density and energy:

\[
F[n'] + \int v(r)n'(r) \, dr \geq E_0.
\] (2.26)

In other words, this means that we can find the ground state density and energy of any number of interacting electrons by minimizing \( E[n] \) in only 3 dimensions! To proceed further we need to find an expression for the universal functional. An early functional is based on the work of Thomas and Fermi on heavy atoms:\textsuperscript{52-54}

\[
F[n] = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \int n^{\frac{5}{3}} \, dr + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} \, dr \, dr'.
\] (2.27)

The first term is an approximate functional for the kinetic energy of non-interacting electrons and the second term represents an effective coulomb repulsion. This approximation turned out to be too crude, failing to reproduce chemical bonding.\textsuperscript{55} This is because the kinetic energy forms a large part of the total energy. Unfortunately an exact kinetic energy functional of the charge density, even for the non-interacting case, has never been derived. Thus there seems to be a difficulty in proceeding from the density. To overcome this problem Kohn and Sham proposed to construct a system of non-interacting electrons, described by single particle wave-functions, that would reproduce the charge density of the original interacting system. For the universal functional they wrote:

\[
F[n] = T_s[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} \, dr \, dr' + E_{xc}[n].
\] (2.28)

The first two terms describe the non-interacting electrons. Although \( T_s \) is written as a functional of the charge density, in reality it is calculated precisely from the single particle wave functions. The last term, is the smallest one, adds all the missing many-body interactions (exchange and correlation). Minimization of \( E[n] \) leads to the well known Kohn-Sham equations that are solved iteratively:

\[
\left[ -\frac{1}{2} \nabla^2 + \int \frac{n(r')}{|r - r'|} \, dr' + v_{xc}(r) + v(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r)
\] (2.29)

where

\[
v_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n}
\] (2.30)
and

\[ n(r) = \sum_{n}^{N} |\varphi_j(r)|^2. \tag{2.31} \]

Kohn and Sham also suggested a form for \( E_{xc} \), known as the local density approximation (LDA).\(^{56}\) Here the space is divided into small elements. The contribution to \( E_{xc} \) from a given element is taken to be the same as from a homogeneous interacting electron gas. The exchange and correlation energies of a homogeneous gas as a function of density are known from stochastic calculations. This is a good approximation for densities that vary slowly in space. More accurate expressions for \( E_{xc} \), denoted as GGA are based on gradient expansions.\(^{57,58}\)

So far we have considered systems where the nuclei are fixed. Once we have calculated the ground state it is actually quite easy to calculate forces acting on the nuclei. Using the Hellmann-Feynman theorem the force on a particular nucleus can be calculated as:

\[ F_{\lambda} = -\frac{\partial E}{\partial \lambda} = \int \Psi^*(\lambda) \frac{\partial \hat{H}}{\partial \lambda} \Psi(\lambda) \, d\tau \tag{2.32} \]

Here \( \lambda \) denotes a component of the force vector. In the Hamiltonian only two terms depend on \( \lambda \): the electron-nuclei and nuclei-nuclei term. To calculate the force we need to know only position of the atoms and the charge density. This allows us to perform molecular dynamics calculations as well as relaxations to find equilibrium structures.\(^{59}\)

Since the original papers of 1964-65, DFT developed into a popular method to study condensed matter. This is probably because of the favorable ratio between accuracy and computational cost. The importance of the theory was recognized by awarding the 1998 Nobel prize in Chemistry to Walter Kohn. The prize was shared with John Pople for his work on wave-function based methods. At present there are several mature DFT programs that are commercial or open source. The field is very much alive. There is an ongoing work on a more accurate description of many-body effects, calculation of excited states and faster algorithms.
Chapter 3

Hydrogenated amorphous silicon

3.1 Introduction

Amorphous semiconductors are an important part of materials science. A lot of effort has been devoted to the research of pure amorphous silicon as a prototype of an amorphous semiconductor. Later on researchers focused on hydrogenated amorphous silicon (a-Si:H) mainly because of its technological importance. The new material brought also new challenges in understanding the peculiar role of hydrogen in the amorphous network. The main advantage of hydrogenated amorphous silicon (a-Si:H) over crystalline silicon lies in its production technique. Thin films of a-Si:H can be deposited over large areas using plasma enhanced chemical vapor deposition. The films can be deposited at low temperatures, thus allowing the use of plastic substrates. The main applications are large area electronic devices such as liquid-crystal displays and solar cells. In the visible part of the spectrum the absorption coefficient of a-Si:H is higher by an order of magnitude than that of crystalline silicon.\textsuperscript{60} The higher absorption coefficient means less material in order to absorb the same amount of light, thus allowing for use of films less than 1 micrometer thick. Amorphous solar cells can be deposited on flexible substrates in a cheap roll-to-roll process.\textsuperscript{61}

Despite the technological importance of a-Si:H many of its properties are still not yet fully understood. These include the local bonding environment of hydrogen, the structure of defects and light-induced degradation.
There were several theoretical studies of a-Si:H in the past.\textsuperscript{62–72} One of the first models of a-Si:H was created by Allan \textit{et al.} using the cluster Bethe-lattice approach.\textsuperscript{62} Another class of methods is based on an a-priori assumption about the amorphous network, such as perfect coordination. A typical example is the bond-switching or WWW algorithm.\textsuperscript{63} An improved version of the algorithm is known to generate high-quality models with a modest computation effort.\textsuperscript{64} In 1985 Car and Parrinello simulated the cooling of liquid silicon to obtain a structure of the amorphous phase.\textsuperscript{65} The calculations were performed at the level of density functional theory. Many of the first-principles studies on a-Si:H follow this procedure,\textsuperscript{66–70} while others are based on a slightly different approach. E.g., Klein \textit{et al.}\textsuperscript{71} 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. Valladares \textit{et al.}\textsuperscript{72} proposed a cooling procedure, where they are using different time steps (not necessarily physical) to control the short range order in the amorphous structure.

The drawback of the “cooling of the liquid” approach is the number of defects it creates. A device quality material has typically a defect concentration of $10^{17}$ \text{cm}^{-3}.\textsuperscript{73} This implies that a supercell containing $10^6$ atoms should have one defect. Smaller supercells should be essentially defect free, i.e. thus all silicon atoms should be four-coordinated and the sample should have a clean band gap without any defect states. This poses a severe challenge to first-principles simulations, as these are restricted by the vast computational cost to very high cooling rates. To our knowledge all previous first-principles studies on a-Si:H were hampered by this difficulty. Obtaining defect-free samples in the computer is crucial for device modeling, e.g., to determine band offsets at interfaces with a-Si:H. In this study we present structures containing low defect concentrations, generated from first-principles molecular dynamics. We demonstrate that it is in fact possible to prepare defect free samples using the “cooling of the liquid” method. Furthermore, we investigate the convergence of the calculated properties with respect to the supercell size, showing that the band edge features are already well described in a relatively small cell of $\sim 72$ atoms. The vibrational density of states is calculated as another confirmation of the correct short range order present in our samples.

This chapter is organized as follows: Technical details are provided in Sec. 3.2. In Sec. 3.3 we describe the thermal procedure used to prepare amorphous structures and technical details of the calculation. In Sec. 3.4
we discuss the effect of the cooling rate on the quality of the structures. The structural and electronic properties of samples prepared by slow cooling are discussed in Sec. 3.5. In Sec. 3.6 we analyze how the properties of the samples change with the supercell size. Section 3.7 focuses on defect structures and their electronic properties. The study of the vibrational density of states is given in Sec. 3.8. Finally, conclusions are presented in Sec. 3.9.

3.2 Technical details

The total energy and forces are calculated within the DFT using a Generalized Gradient Approximation (GGA).\textsuperscript{57} We use the Vienna Ab initio Simulation Package (VASP).\textsuperscript{40,41} Electron-ion interactions are described using the projector augmented wave method (PAW).\textsuperscript{42,74} We use the standard PAW potentials distributed with the VASP package. The silicon potential has two reference energies for the s and p channel and one energy for the d channel. The hydrogen potential has two reference energies for the s channel and one energy for the p channel. The \textit{1s}^2\textit{2s}^2\textit{2p}^6 electrons of silicon are kept frozen in the core. The kinetic energy cut-off is set to 200 eV. During the whole MD run and the relaxation, we use only the $\Gamma$ point for Brillouin zone sampling. The partial occupancies are determined by the Methfessel-Paxton method\textsuperscript{75} with a smearing width of 0.2 eV. For calculations on the relaxed structures we use a 5\times5\times5 Monkhorst-Pack mesh\textsuperscript{76} for the Brillouin Zone sampling and a Gaussian broadening of 0.05 eV.

The highest vibrational frequency which can occur during the simulation is due to the vibration of the hydrogen molecule. The silicon-hydrogen stretching mode has the second highest frequency (\textit{\~2100 cm}^{-1}).\textsuperscript{77} The average calculated value is 2087 cm\textsuperscript{-1} (depending on the local environment). We set our time step to 1 fs which proves to be sufficient to describe the Si-H stretching mode. The integration of the vibrational motion of the hydrogen molecule using this time step is rather crude. However the time step of 1 fs is a reasonable compromise between computational cost and accuracy.

3.3 Preparation of the structure

Hydrogen plays a vital role in saturating dangling bonds and removing electronic defect states inside the band gap. A typical device quality ma-
CHAPTER 3. AMORPHOUS SILICON

Material for solar cell applications has a hydrogen concentration of 11 at.%.

We start the preparation procedure with a periodically repeated cubic supercell containing 64 silicon and 8 hydrogen atoms. The supercell is built of 8 \( (2 \times 2 \times 2) \) c-Si:H cells each comprising eight silicon and one hydrogen atom. The c-Si:H cell is in fact a cubic unit cell of crystalline silicon with one hydrogen atom in the middle. The side of the supercell is set to 11.062 Å to reproduce the experimental density of 2.20 g/cm\(^3\).

The heating and cooling of the structure was done by velocity rescaling on every MD step. The thermal procedure begins at 300 K. The velocities are initialized randomly according to a Maxwell-Boltzmann distribution. The structure is than heated to 2370 K in 1.5 ps which corresponds to a heating rate of 1.380 K/fs. At this temperature the system is a liquid. We find that the liquid sample is a metal with no trace of a gap in the density of states. This is consistent with previous calculations. In order to destroy any trace of crystallinity we let the system evolve for 4 ps. Subsequently the system is cooled back to 300 K.

We apply three different cooling procedures and study their effect (see Fig. 3.1). In the first and quickest procedure the cooling rate is identical to the heating rate (1.380 K/fs). We’ll refer to this rate as the “fast” cooling rate. In the second we cool the sample to 300 K in 15 ps resulting in a ten times slower rate (0.138 K/fs). This rate is referred to as the “normal” cooling rate. In the last cooling procedure we are actually using three different rates. From 2370 K to 1818 K we follow the 0.138 K/fs rate, from 1818 K to 783 K we apply the “slow” rate of 0.023 K/fs and finally from 783 K to 300 K we apply again the fast rate (1.380 K/fs). The usage of three different rates is motivated by preparing a high quality amorphous structure in a short time. In the first temperature interval (corresponding to the fast cooling rate) the silicon atoms still exhibit a strong liquid-like behavior. In the second interval, being the most important, the rate used is as small as possible to allow even improbable relaxation events to occur. In the final temperature interval the atoms exhibit only vibrational movement with almost no chance of a further structural relaxation. Consequently we use the fastest cooling rate to save computer time. As can be seen in Fig. 3.1 we prepared a total of five different samples using the slow cooling rate. We will denote them as A, B, C, D and E.

After reaching room temperature the system is evolved for 0.5 ps (still coupled to the thermostat) to calculate structural averages of, e.g., the pair-distribution function, bond angle distribution function and static
3.4. EFFECT OF THE COOLING RATE

Figure 3.1: The heating and cooling scheme used to prepare three samples with fast, normal and slow cooling rate. The five slow quench samples are marked with letters A, B, C, D and E.

structure factor. After calculating the structural averages the amorphous structure is quenched using the conjugated gradient method and electronic properties are calculated.

3.4 Effect of the cooling rate

To examine the effect of the cooling rate on the quality of the amorphous structure we employ three distinct cooling procedures. We compare the different resulting samples in terms of their structure, number of defects and electronic properties. Thus we can assess the effect of the slower cooling rates.

A useful measure of short range order in amorphous structures is the pair-distribution function $g(r)$. It gives the probability of finding two atoms at a distance $r$ apart. For a binary system like a-Si:H there are three partial pair-distribution functions i.e. $g_{Si-Si}(r)$, $g_{Si-H}(r)$ and $g_{H-H}(r)$. We show the silicon–silicon pair-distribution function after the different cooling rates in Fig. 3.2. We observe that slower cooling results in better-defined peaks with higher values of the first and second maximum of $g_{Si-Si}(r)$. With slower cooling rates the value of the first minimum in $g_{Si-Si}(r)$ is decreasing towards zero.

To define other correlation functions we need to determine a cutoff distance for the silicon–silicon and the silicon–hydrogen bond. If a dis-
Figure 3.2: Partial pair-distribution function Si-Si of three structures prepared by fast (black line), normal (red line) and slow cooling rate (gray line). The distribution function was determined for a system at 300 K.

distance between two atoms is smaller than the cutoff distance, they are considered to be bonded. The cutoff distance of the silicon–silicon bond was set to 2.76 Å corresponding to the position of the first minimum in $g_{Si-Si}(r)$. Similarly the cutoff distance of the silicon–hydrogen bond was set to 1.79 Å matching the position of the first minimum in $g_{Si-H}(r)$. The cooling rate does not change the position of the first minimum in $g_{Si-Si}(r)$ and $g_{Si-H}(r)$, which justifies the usage of the same cutoff distances for all the prepared samples.

The average Si–Si coordination number $N_c$ for the normal and slow cooling rates approaches the expected value for a-Si:H with 11 at. % of hydrogen (see Table 3.1). If we suppose that a-Si:H has a total coordination number of 4, i.e. the material is defect free and that the hydrogen atoms are used solely to saturate dangling bonds. Then we should have a coordination number of 3.89 for a material containing 11 at. % hydrogen. The mean first neighbor distance $r_1$ decreases with slower cooling and approaches the experimental values (see Table 3.3). A decreasing trend is also observed for the second neighbor distance $r_2$. The parameters related to the second neighbor peak are calculated from distances between two silicon atoms bonded to a common atom. The mean values are calculated as averages over 500 MD steps with the samples at 300 K. The deviations of the first and second neighbor distances are due to static disorder and were calculated at 0 K. The experimental values of $\sigma_1$ and $\sigma_2$ are usually
3.4. EFFECT OF THE COOLING RATE

Table 3.1: Structural properties of samples prepared by fast, normal and slow cooling rates: coordination number $N_c$, mean first neighbor distance $r_1$, deviation of the first neighbor distance $\sigma_1$, mean second neighbor distance $r_2$, deviation of the second neighbor distance $\sigma_2$, mean bond angle $\theta$ and deviation of the bond angle $\sigma_\theta$. The mean values and the coordination number are calculated at 300 K, the deviations refer to static disorder and are calculated at 0 K. The values of the slow rate are averaged over the five samples.

<table>
<thead>
<tr>
<th>structure</th>
<th>$N_c$</th>
<th>$r_1$</th>
<th>$\sigma_1$</th>
<th>$r_2$</th>
<th>$\sigma_2$</th>
<th>$\theta$</th>
<th>$\sigma_\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast</td>
<td>3.97</td>
<td>2.417</td>
<td>0.058</td>
<td>3.855</td>
<td>0.401</td>
<td>107.731</td>
<td>16.55</td>
</tr>
<tr>
<td>normal</td>
<td>3.86</td>
<td>2.386</td>
<td>0.061</td>
<td>3.852</td>
<td>0.353</td>
<td>108.891</td>
<td>14.25</td>
</tr>
<tr>
<td>slow(average)</td>
<td>3.89</td>
<td>2.377</td>
<td>0.049</td>
<td>3.840</td>
<td>0.326</td>
<td>108.894</td>
<td>13.57</td>
</tr>
</tbody>
</table>

obtained by fitting to the Si-Si pair-distribution peak. The experimental distributions are broadened by thermal vibration and by real space resolution. To calculate the static deviations it is then necessary to subtract the thermal and experimental broadening of a c-Si sample. Note, that although this method is often used, it is an approximation.

Further, we calculate the bond angle distribution function, which gives the distribution of angles between two silicon–silicon bonds connected to a common silicon atom (see Fig. 3.3). The bond angle distributions of samples obtained via the slow cooling rate are essentially identical (In Fig. 3.3 we depict only that of sample A). The peak centered around the tetrahedral bond angle ($\sim 109.5^\circ$) narrows with slower cooling rate. The bond angle deviation $\sigma_\theta$ changes from 16.55$^\circ$ to 13.57$^\circ$ for fast and slow cooling rates respectively. Again these values are due to static disorder and were calculated at 0 K. Note that the sample prepared by the fast cooling rate has also a peak at 55$^\circ$. This is a residue of the metallic bonding in the liquid. As was shown by Štich et al.\textsuperscript{79} this peak can reach the same intensity as the tetrahedral one in liquid silicon.

The healing power of slow cooling is even more visible in the electronic properties. The number of structural defects responsible for the in-gap states decreases with slower cooling (see Table 3.2). This trend can be also followed in the calculated density of states, see Fig. 3.4. Here the DOS of the different samples are aligned for clarity. The zero of the energy scale is chosen to coincide with the average of the Kohn-Sham eigenvalues of all the occupied states. Note that the slow quench structure has neither
Figure 3.3: The Si–Si–Si bond angle distribution of three structures prepared by fast (black line), normal (red line) and slow (gray line) cooling rates (sample A).

Table 3.2: Types of neighboring environments for three structures prepared by fast, normal and slow cooling rates. The expression Si$_3$H$_1$ denotes that the given atom has a total number of four neighbors, three of which are silicon atoms and one is a hydrogen atom.

<table>
<thead>
<tr>
<th>structure</th>
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<th>Si$_3$H$_0$</th>
<th>Si$_3$H$_1$</th>
<th>Si$_4$H$_0$</th>
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</tbody>
</table>
3.5. STRUCTURES OBTAINED BY SLOW COOLING

Figure 3.4: Density of states of three structures prepared by fast (black line), normal (red line) and slow (gray line) cooling rates (sample A). The DOS functions are aligned for clarity. The positions of the Fermi levels are: 3.61 eV, 3.52 eV and 3.27 eV for the fast, normal and slow cooling rate respectively.

structural defects nor electronic defect states in the gap. The tendency of improving the quality of the structure with slower cooling is exactly what one would intuitively expect. What is not so obvious, is whether the rate of the order of 0.01 K/fs is sufficient. The correlation functions of the slow quench sample however reproduce the experimental ones and the sample is essentially defect free. This suggests that the slow cooling rate is indeed sufficient to prepare realistic amorphous structures.

3.5 Structures obtained by slow cooling

All five structures prepared by slow cooling (A, B, C, D and E) start from different liquid configurations separated in time by 2 ps at the temperature 2370 K (see Fig. 3.1). The pair-distribution functions as well as the static structure factors are averaged over the five slowly quenched samples and compared with neutron diffraction measurements.\(^{45}\)

The static structure factor is a quantity proportional to the diffracted intensity in an X-ray or neutron diffraction experiment. For a binary compound there are three partial static structure factors. We calculate
them according to the definition of Ashcroft and Langreth:

\[
S_{ij}(q) = \frac{1}{\sqrt{N_i N_j}} \left[ \left\langle \sum_{\mu} \sum_{\nu} e^{-i\mathbf{q} \cdot (\mathbf{R}_{i\mu} - \mathbf{R}_{j\nu})} \right\rangle - \delta_{\mathbf{q}, \mathbf{0}} \right],
\]

(3.1)

where \(N_i\) and \(N_j\) denote the number of atoms of species \(i\) and \(j\) respectively, \(\mathbf{R}\) are the position vectors of the atoms and \(\mathbf{q}\) is a vector in reciprocal space. The averaging is performed over different \(\mathbf{q}\) which have the same length (we consider only vectors \(\mathbf{q}\) on the reciprocal lattice). The resulting structure factor is than averaged over different configurations during a 0.5 ps time interval at the temperature of 300 K. As seen in Fig. 3.5 the agreement between theoretical and experimental silicon–silicon structure factor is good. We are able to reproduce the first two peaks as well as the following peaks up to 15 \(\text{Å}^{-1}\). The agreement is worse for the other partial static structure factors. This is due to the very small number of hydrogen atoms, resulting in a poor statistics. Another source of discrepancy is that we treat the hydrogen atom as a classical particle. Note that Bellissent et al. use a material with 16 at. % of hydrogen.

The pair-distribution \(g_{\alpha\beta}(r)\) for a binary compound is defined as the number of particle pairs \(N_{\text{sys}}(r)\) in the system, relative to the number of pairs we would find in an ideal gas. The number of \(\beta\) atoms that are at the distance \(r\) apart from atoms of type \(\alpha\) is

\[
N_{\text{sys}}(r) = \sum_{I=1}^{N_\alpha} \sum_{J=1}^{N_\beta} \delta(r - |\mathbf{R}_I - \mathbf{R}_J|),
\]

(3.2)

where \(\mathbf{R}\) are the position vectors of atoms and \(N\) is the number of atoms of a particular species. For atoms that are randomly distributed in space, we get

\[
N_{\text{gas}}(r) = N_\alpha (4\pi r^2 \frac{N_\beta}{V}),
\]

(3.3)

where \(V\) is the volume of the system. Thus the theoretical pair-distributions \(g_{\alpha\beta}(r)\) are calculated according to the expression:

\[
g_{\alpha\beta}(r) = \frac{V}{4\pi r^2 N_\alpha N_\beta} \sum_{I=1}^{N_\alpha} \sum_{J=1}^{N_\beta} \delta(r - |\mathbf{R}_I - \mathbf{R}_J|).
\]

(3.4)
Figure 3.5: Partial static structure factors averaged over five slow quench samples (black line) and compared to neutron scattering measurements (red line). All structure factors use the Ashcroft and Langreth formalism. Both curves refer to systems at 300 K.
The experimental pair-distributions are obtained by Fourier transforming the static structure factor. Comparing the calculated and measured pair-distributions in Fig. 3.6 we find a very good agreement in the peak positions. However, there is a major difference in the intensity of the first peak, in both, the Si–Si and Si–H partials. This discrepancy is mainly due to two reasons. Firstly the peak height depends on the experimental resolution. We studied several experimental Si-Si pair-distribution as measured by Bellissent et al., Fortner et al., Kugler et al. and Laaziri et al. We observe that increasing the maximum momentum value $Q_{\text{max}}$ from 16 up to 55 Å$^{-1}$ considerably sharpens the peak and increases its height. The samples in these measurements were not identical, but sufficiently similar to warrant this comparison.

The second source of discrepancy is the neglect of the quantum nature of the nuclei. So far we have treated the atomic nuclei as classical particles, thus overestimating the peak heights. Here we follow the method outlined by Giacomazzi et al. to account for the quantum effects. The delta function in Eq. 3.4 is replaced by a Gaussian function normalized to one and with a variance of

$$\sigma_{ij}^2 = \langle (\mathbf{d} \cdot (\mathbf{u}_i - \mathbf{u}_j))^2 \rangle,$$

(3.5)

where $\mathbf{d}$ is a unit vector pointing in the direction of $\mathbf{R}_j - \mathbf{R}_i$. $\mathbf{R}_I$ and $\mathbf{R}_J$ denote equilibrium positions of the $I$th and $J$th atoms respectively. $\mathbf{u}_I$ is the displacement of the $I$th atom with respect to $\mathbf{R}_I$. The brackets $\langle \ldots \rangle$ symbolize a thermal average. The various contributions are obtained as follows:

$$\langle u_{Ii}u_{Jj} \rangle = \sum_n \frac{\hbar}{\omega_n} \frac{\xi_{ii}^n}{\sqrt{M_I}} \frac{\xi_{jj}^n}{\sqrt{M_J}} \left[ n_B(\hbar\omega_n) + \frac{1}{2} \right],$$

(3.6)

where the $i$ and $j$ subscripts denote Cartesian components. The sum runs over vibrational modes $n$ with eigenmodes $\xi^n$ and eigenfrequencies $\omega_n$. The vibrational modes are calculated via the finite differences method available in the VASP package (see, e.g., Kresse et al.). $M_I$ is the mass of the $I$th atom. The Boson occupation number $n_B$ is calculated according to

$$n_B(\hbar\omega) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1},$$

(3.7)

The fact that the experimental static structure factors are measured over a finite interval in reciprocal space, results in unphysical negative values of the pair-distribution function at small distances.
Figure 3.6: Partial pair-distributions averaged over 500 MD configurations (black solid line), calculated pair-distributions with quantum corrections (red dashed line) and neutron scattering measurements (gray solid line). Both types of calculated curves are averages over five slow quench samples. All curves refer to systems at 300 K.
where \( k_B \) is the Boltzmann constant and \( T \) is the temperature of the system.

The calculated pair-distributions that take quantum effects into account are depicted in Fig. 3.6. The Si–Si partial distribution remains unchanged due to the relatively high mass of silicon atoms. We do, however, see a considerable change in the Si–H distribution, where the height of the first peak decreases to a third of the original one. Thus after applying the quantum corrections we get a much better agreement with experiment. However, the calculated peaks are still above the measured ones, due the finite experimental resolution.

Parameters like the coordination number (area under the first peak) and average bond length are less affected by experimental resolution. It is thus more meaningful to compare the coordination number and average bond length than the peak intensities (for the first peak). Unfortunately Bellissent et al. did not publish coordination numbers for their measurement. We summarize several calculated and experimental structural parameters for the Si–Si partial distribution in Table 3.3. The average Si–Si coordination number coincides with the expected value for a defect free material containing 11 at. % of hydrogen. We note that the experimental values differ significantly. Laaziri et al. showed that scattering data out to at least 40 Å\(^{-1}\) is necessary to reliably determine the value of \( N_c \). The relative differences between the measured values of \( r_1 \) are approximately 1 %. The same holds for differences between our results and the experiment. The calculation overestimates the static deviation of the first neighbor distance \( \sigma_1 \). The comparison to experimental values indicates that the model contains more static disorder, although some of the slow quench samples fall into the uncertainty range of \( \sigma_2 \) reported by Wakagi et al. The calculated average second neighbor distance \( r_2 \) coincides with neutron scattering measurements\(^{45,88}\) and with the crystalline silicon value. The value reported by Laaziri et al. is lower than the other experimental values. Laaziri et al. note that this can be due to contributions from the third peak in the Si–Si pair-distribution that affect the peak fitting parameters. Consequently the bond angle reported by Laaziri et al. is lower than values reported by Schülke et al., Bellissent et al.\(^{45}\) and is lower than the tetrahedral angle in c-Si (109.47°). The bond angle deviation \( \sigma_\theta \)

\(^{1}\text{The quantum effects would be bigger at low temperature. Feldman et al. obtained a significant broadening, for pure amorphous silicon at 10K, originating from quantum mechanical nature of the nuclei.}\)
Table 3.3: Properties of the five samples prepared by slow cooling rate: mean first neighbor distance $r_1$, deviation of the first neighbor distance $\sigma_1$, mean second neighbor distance $r_2$, deviation of the second neighbor distance $\sigma_2$, coordination number $N_c$, mean bond angle $\theta$, deviation of the bond angle $\sigma_\theta$ and band gaps $E_{gap}$ compared to experimental values. Author names are followed by hydrogen concentrations in atomic %.

The mean values and the coordination number are calculated at 300 K, the deviations refer to static disorder and are calculated at 0 K.

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<td>108.89</td>
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<td>Filipponi, 84 8</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>Vignoli, 85 12</td>
<td>2.37 ±0.04</td>
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<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Wakagi, 86 12.8</td>
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<td>0.038±0.008</td>
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<td>–</td>
</tr>
<tr>
<td>Schülke, 87 33</td>
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<td>–</td>
<td>3.86±0.01</td>
<td>0.187±0.005</td>
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<th>$\sigma_\theta$</th>
<th>$E_{gap}$ (eV)</th>
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<td>–</td>
<td>–</td>
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<td>Vignoli, 85 12</td>
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<td>8.7</td>
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<tr>
<td>Wakagi, 86 12.8</td>
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<td>–</td>
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<td>109.5±1.0</td>
<td>7.9±0.4</td>
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</tbody>
</table>
measured by Schülke is the lowest value compared to measurements of Wakagi et al. and Vignoli et al. This can probably be attributed to the large amounts of hydrogen (33 at. %) present in the sample. Vignoli et al. and Wakagi et al. obtain the bond angle deviation in an indirect way using the Raman spectra. They use a model, where the angle deviation depends linearly on the width of the TO peak. Vignoli et al. measured a deviation of 8.7° for an a-Si:H sample containing 12 at. % of hydrogen. Laaziri et al. obtain the bond angle deviation from the width of the second peak in the silicon pair-distribution. They subtract the thermal disorder and experimental resolution utilizing the values measured on c-Si samples. Laaziri et al. report that the angle deviation value of 9.63° agrees well with previous studies. However they point out that the result has to be treated with caution, since the second peak can contain contributions from the third peak and this can affect the fitting parameters. We note that our average value of the bond angle deviation is lower compared to previous calculations of Gupte et al. (21.7°) and Klein et al. (16.6°). The trend that theoretical calculations (including our calculation) overestimate the bond angle deviation is rather clear. The same trend is observed in the deviation of the second neighbor distance since these two parameters are closely connected. We would like to point out that the angle deviation is a very sensitive parameter. The five slow quench samples exhibit a significant variation in the angle deviation. On the contrary other parameters are very similar.

The experimental information available on the Si–H partial distribution is more sparse than on the Si–Si one. The calculated position of the first peak is found to be 1.51 Å. We note that the calculated value of 1.51 Å is identical to the calculated silicon–hydrogen bond length in the silane molecule. The calculated hydrogen–hydrogen pair-distribution (not-shown) has a peak at 0.75 Å, corresponding to the hydrogen molecule bond. Hydrogen molecules are found in samples A and D. The statistics in the hydrogen–hydrogen pair-distribution function is very poor, rendering any comparison with the experiment unreliable.

The band gap values for all slowly quenched samples are summarized in Table 3.3. The reported band gaps are calculated as a difference between the energy of the lowest unoccupied state and the highest occupied state, leaving out the defect states. Defect states are identified on the basis of their localized nature. The average band gap is found to be 0.92 eV with a standard deviation of 0.10 eV. The experimental value for a device
3.6 Convergence of the supercell size

To study the effect of the supercell size on the calculated properties we performed a calculation on a bigger supercell containing 216 silicon and 27 hydrogen atoms. The preparation procedure is analogous to the preparation of smaller supercells by slow cooling, employing the same rates. The initial supercell is now build of 27 \((3\times3\times3)\) c-Si:H cells. The silicon–silicon pair-distribution of the small and big cell closely resemble each other (see Fig. 3.7). They both reproduce the experimental curve up to a distance of 5.5 Å, with correct positions of the first and second peak. The calculated position of the third peak (only visible in the big cell) is a bit higher than the experimental value. The coordination number of the big sample is 3.87, a value close to the averaged value of the small samples (3.89). The mean first neighbor distance is 2.374 Å with a static deviation of 0.041 Å. The mean second neighbor distance is found to be 3.838 Å with a static deviation of 0.302 Å. Thus we find that the mean values of the first and second neighbor distance do not change significantly if one uses bigger supercells. The static deviations of the big supercell are found to be lower than the average deviations of the small supercells. It is however difficult to draw any conclusions from that, since the deviation values vary considerably among the small samples. Note that for example sample C has a lower \(\sigma_1\) value than the big sample and sample B has a lower \(\sigma_2\) value than the big sample. The average bond angle of the big sample \((108.89^\circ)\) is identical to the averaged value of the small samples. By analogy to \(\sigma_2\), the bond angle deviation of the big sample is lower than the average of the small samples. The value of \(\sigma_\theta\) due to static disorder is 12.54°. The band gap of the big sample is found to be 0.90 eV, a value close to the average band gap of the smaller samples. The positions of the first and second peak in the silicon–hydrogen pair-distribution are 1.51 Å and 3.15 Å respectively, in both the small and big sample.

The largest discrepancies between distribution functions are found in
Figure 3.7: Partial pair-distribution functions of the small supercell (black solid line), big supercell (red dashed line) compared to neutron scattering measurements (gray solid line). Theoretical curves contain quantum corrections calculated at 300 K.
the hydrogen–hydrogen partial. The first peak, due to the H$_2$ molecules is present in the models but not in the experimental curve. In addition to neutron scattering, the structure of hydrogen in a-Si:H was studied by nuclear magnetic resonance (NMR). It is observed that hydrogen exists in an isolated and clustered form.$^{90-93}$ Isolated H atoms give rise to a narrow Lorentzian while clustered atoms induce a broad Gaussian in the NMR spectrum. The full width at half maximum of the Gaussian can be approximated as:$^{92}$

$$\sigma(\text{kHz}) = 190 \left( \frac{1}{N} \sum_{i,j=1}^{N} r_{ij}^{-6} \right)^{\frac{1}{2}},$$  \hspace{1cm} (3.8)

where the subscripts $i$ and $j$ are indexes of H atoms, $r_{ij}$ is the distance between atoms in angstroms and $N$ is the total number of atoms. We have calculated $\sigma$ for the big a-Si:H cell and find that it fluctuates between 16 and 28 kHz. The values were obtained during a 0.5 ps MD run at 300 K. Atoms forming the hydrogen molecule were excluded from the calculation. A visual inspection of the model reveals hydrogen clustering and the relatively high $\sigma$ values confirm this conclusion. In case the hydrogen is distributed uniformly (on a cubic lattice) it leads to a $\sigma$ value of 3 kHz. In an experimental study Gleason et al. report values around 30 kHz.$^{91}$

Due to the structural disorder present in amorphous semiconductors, states in the vicinity of the valence and conduction band edges are localized and form the so called “band tails”. Localization of states in the presence of disorder was predicted in the early model by Anderson.$^{94}$ Band tails are well established experimentally by photoemission, optical absorption and electrical transport measurements.$^{73}$ In fact electronic properties of amorphous semiconductors, which differ considerably from their crystalline counterparts, are due to the band tails. Recent work on realistic models of pure amorphous silicon provides a link between the atomic structure and band tails. It was demonstrated that short and long bonds are responsible for the valence and conduction band tail states respectively.$^{95,96}$ Both groups of bonds connect to larger aggregates. Short bonds form 3D clusters, while long bonds connect into 1D filaments. It is also suggested that this mechanism might be generally valid for amorphous semiconductors.$^{97}$

In order to better characterize the band tails, we employ the so-called participation ratio $p_i$, which is a measure of localization of the eigenstates $\psi_i$. It is calculated by projecting the wave function $\psi_i$ onto spherical
Chapter 3. Amorphous Silicon

Participation ratio vs. energy of the Si$_{216}$H$_{27}$ supercell. Each dot represents a distinct Kohn-Sham state. The Brillouin Zone sampling was done with a $5 \times 5 \times 5$ Monkhorst-Pack mesh.

The participation ratio is defined as follows (see, e.g., Ref. 98):

$$p_i = \left( \sum_{j=1}^{N} \sum_{l=1}^{3} c_l^2(R_j) \right)^2 \left( N \sum_{j=1}^{N} \sum_{l=1}^{3} c_l^4(R_j) \right)^{-1}.$$  \hspace{1cm} (3.9)

The sums run over angular-momentum components $l$ and over each atom with coordinates $R_j$. The order of the spherical harmonics function $m$ is already absorbed in the expansion coefficients $c_l$. According to this definition $p_i \sim 1$ for a delocalized state (e.g. plane wave) and approaches the value $N^{-1}$ for a localized state, where $N$ is the number of atoms. In Fig. 3.8 we show the participation ratio of every electronic state in our big supercell. Different regimes of localization, typical of an amorphous semiconductor, can be distinguished: The valence band region (from -10 eV to -1 eV), valence band tail region (from -1 eV to -0.6 eV), band gap region (from -0.6 eV to 0.3 eV) with very localized defect states, conduction band tail region (from 0.3 eV to 1 eV) and the conduction band region (from 1 eV) with delocalized states.

3.7 Structural and electronic defects

As discussed previously, two samples do not contain any defects. This is a considerable improvement over previous models prepared with the cool-
3.7. **STRUCTURAL AND ELECTRONIC DEFECTS**

Table 3.4: Types of local environments of structures prepared by slow cooling. The expression $\text{Si}_3\text{H}_1$ denotes that the given silicon atom has a total number of four neighbors, three of which are silicon atoms and one is a hydrogen atom. The last column gives the number of $\text{H}_2$ molecules in the sample.

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</tbody>
</table>

From liquid approach. On the other hand a small number of defects can give valuable information about the structure and electronic properties of defects in a-$\text{Si}:\text{H}$. Three out of five samples (B, D, E) contain one dangling bond (undercoordinated atom) and one floating bond (overcoordinated atom) each. The big supercell contains one dangling bond and two hydrogens in a bond-centered (BC) position. Samples A and C, have no structural defects (see Table 3.4). The calculated densities of states of these defect-free samples is shown in Fig. 3.9.

Even though there is no one-to-one correspondence between a structural defect and an electronic defect state (as pointed out by Drabold et al.\textsuperscript{99}), we were able to assign almost all electronic defects to defect atoms.\textsuperscript{9} In Fig. 3.10 we show the calculated density of states for the samples containing defect states inside the gap. The defect state B1 is a dangling bond with the charge density localized on a 3-fold coordinated atom. The defect state B2 is a floating bond with the charge density centered around a 5-fold coordinated atom. In this case the charge density is pushed towards the neighboring atoms, contrary to the dangling bond defects, where it is localized on the defect atom itself. This finding is consistent with previous calculations.\textsuperscript{100} The situation is very similar in the case of sample D. The D1 state is a dangling bond with charge density localized on a 3-fold coordinated atom. The D2 state is a floating bond.

\textsuperscript{9}The distinction between a defect state and a band tail state is based on the degree of localization. We define a threshold value of 0.1, since a vast majority of the wave functions that contribute to a defect state have smaller participation ratios.
Figure 3.9: Calculated density of states of the slow quench samples: sample A (gray line), sample C (red line) and c-Si (black line). The values for c-Si were multiplied by a factor of 100. The zero of energy was chosen at the top of the valence band edge.

Figure 3.10: Calculated density of states of the slow quench samples containing in-gap states: sample B (red line), sample D (gray line), sample E (red line) and sample F (gray line). The sample F is the big cell. The density of states of the samples B and D are shifted for clarity. The DOS functions are aligned for clarity. The Fermi levels are positioned at: 3.39 eV, 3.42 eV, 3.22 eV and 3.75 eV for the samples B, D, E and F respectively.
with the charge density localized around a 5-fold coordinated atom. The interpretation becomes more difficult in sample E. For the E1 state it is difficult to decide whether it is a dangling or a floating bond. In this case the defect structures share atoms and the charge density of the E1 state is contributing to both of them. The state E2 is a dangling bond with the charge density centered on the undercoordinated atom. Sample F (the big cell) contains three defect states. The F1 state is a dangling bond, the states F2 and F3 are due to BC hydrogen. The BC hydrogen defect was proposed by Fish and Licciardello\cite{101} and was found also in previous MD simulations.\cite{69} The average Si–H bond length is found to be 1.71 Å and the average Si–H–Si angle is 148.4°. The charge density of the interstitial hydrogen defect is distributed equally between the two Si–H bonds and is localized closer to the silicon atoms.

3.8 Vibrational density of states

The vibrational density of states was calculated for each of the five samples resulting from slow cooling. We used the finite differences method (see, e.g., Kresse et al.\cite{82}) in which all the atoms were displaced by 0.01 Å in the direction of each Cartesian coordinate, both positive and negative. For each displacement forces are calculated as a derivative of the total energy and the dynamical matrix is obtained. The diagonalization provides us with eigenfrequencies of the particular modes. These were broadened with Gaussians with a width of 0.1 eV.

Experimentally the vibrational density of states can be obtained from inelastic neutron scattering measurements. The situation is complicated by the large neutron scattering cross-section of hydrogen compared to that of silicon. As a result the spectrum of a-Si:H is dominated by the hydrogen vibrations. To overcome this problem Sinclair and co-workers performed also measurements on deuterated samples, replacing the 22 % of hydrogen by deuterium.

In Fig. 3.11 we compare our calculated vibrational DOS with the experimental DOS by Sinclair et al.\cite{102} The region from 0 cm\(^{-1}\) to 550 cm\(^{-1}\) is due to vibration of the silicon network. There are two prominent peaks at 150 cm\(^{-1}\) and 460 cm\(^{-1}\). These are the transverse acoustic and transverse optical modes, which are also present in crystalline silicon. There were several studies on pure a-Si\cite{65,79,103–107} giving essentially the same results, although they can differ in the exact peak positions. Note that the
peak at 460 cm\(^{-1}\) is highly asymmetric. This is probably because it is a superposition of the transverse optical mode and the longitudinal modes.

The region from 530 cm\(^{-1}\) to 750 cm\(^{-1}\) is due to SiH wagging, SiH\(_2\) wagging and SiH\(_2\) twisting modes. The frequency regions of the particular modes overlap and depend on the local environment. The experimental peak due to this group of modes is located at 640 cm\(^{-1}\) and is much more noticeable. The peak at 850 cm\(^{-1}\) is arising from a SiH\(_2\) bending (scissors) mode and is also clearly visible in the experimental spectrum. Sinclair\ et\ al.\ resolved the peak in the hydrogenated sample at 1280 cm\(^{-1}\) as a second overtone of the SiH\(_n\) rocking and wagging mode. The SiH stretching modes have frequencies from 1810 cm\(^{-1}\) to 2170 cm\(^{-1}\). The stretching frequencies of the SiH\(_2\) group have higher frequencies from 2070 cm\(^{-1}\) to 2140 cm\(^{-1}\). The large spread of frequencies in the stretching modes is also visible in the experiment. The mode with the highest frequency is the H\(_2\) stretching mode from 4150 cm\(^{-1}\) to 4190 cm\(^{-1}\).

As mentioned above the big supercell contains two hydrogen atoms in a BC position. This should give rise to unique modes in the vibrational density of states. We calculated their frequencies in the big cell allowing the two hydrogens, the four silicon atoms making up the bridges and their nearest neighbors to move. This should be a reasonable approximation since a hydrogen atom is \(\sim\)28 times lighter than a silicon atom. The Si\(_2\)H
wagging mode has a frequencies from $620 \text{ cm}^{-1}$ to $670 \text{ cm}^{-1}$, the $\text{Si}_2\text{H}$ bending mode has frequencies from $750 \text{ cm}^{-1}$ to $800 \text{ cm}^{-1}$. These modes overlap with the $\text{SiH}_n$ wagging and bending modes, thus will be difficult to observe. However the $\text{Si}_2\text{H}$ stretching frequencies are $1050 \text{ cm}^{-1}$ and $1410 \text{ cm}^{-1}$ and are clearly separated from all the $\text{SiH}_n$ modes.

### 3.9 Conclusions

First-principles molecular dynamics simulations of $\text{a-Si:H}$ were carried out. We examined the effect of the cooling rate on the quality of the amorphous structure. A substantial improvement of structural and electronic properties was found with slower cooling. The slow cooling rate and the size of the $\text{Si}_{64}\text{H}_8$ supercell seem to be sufficient to prepare realistic amorphous structures, with low defect concentrations. Further, we obtained a good agreement with the experimental static structure factor and pair-distribution functions from neutron scattering measurements. Other structural properties like the coordination number $N_c$, mean nearest-neighbor distance $\bar{r}$, RMS deviation of the bond length $\sigma_r$ differ by no more than 1% compared to values measured by EXAFS. The average DFT band gap is found to be $0.92 \text{ eV}$, a value higher than the DFT band gap in crystalline silicon. Interestingly, the simulations reveal that the presence of hydrogen molecules in $\text{a-Si:H}$ is possible. The calculations performed on a big supercell give similar structural and electronic properties of the amorphous network, facilitating the use of smaller supercells. Participation ratio as a function of energy demonstrates the localized nature of band tail states. Two out of five slow quench samples contain neither structural defects nor electronic defect states in the gap. In the other the samples we find dangling and floating bond defects and couple them to undercoordinated and overcoordinated atoms respectively. The big cell sample contains hydrogen in a bridging position, giving states in the gap. The calculated vibrational density of states compares well to the one obtained by inelastic neutron scattering. The stretching frequency of the hydrogen bridge is different from the stretching, bending and wagging frequencies of the $\text{SiH}$ and $\text{SiH}_2$ groups, thus should be visible by IR spectroscopic techniques.
Chapter 4

Defects in hydrogenated amorphous silicon

4.1 Introduction

Hydrogenated amorphous silicon (a-Si:H) is a material with promising applications in large area electronic devices such as solar cells and displays. The main advantage over crystalline silicon is in its production technique. a-Si:H can be deposited cheaply over large areas and on flexible substrates.\(^\text{61}\)

Theoretical studies of a-Si:H are mostly focused on generating realistic structural models of the amorphous network. The calculations involve molecular dynamics simulations of cooling a liquid. The level of approximation in obtaining forces acting on atoms ranges from classical model potentials\(^\text{108–111}\) and tight-binding\(^\text{71,112,113}\) to density functional theory (DFT).\(^\text{66,72,114}\) Another group of methods assumes a priori a certain property of the amorphous network. The bond-switching algorithm of Wooten et al.\(^\text{63}\) generates models of pure a-Si with silicon atoms that are always 4-fold coordinated. Reverse Monte Carlo methods can generate models that exhibit the measured pair-distribution functions.\(^\text{47}\) Note that none of the above methods attempts to simulate the process by which thin films of a-Si:H are deposited.

In this work we use the cooling from liquid approach within the DFT approximation. Although DFT calculations are computationally demanding we feel that this level of precision is necessary to account for the different chemical environments during the thermal procedure. It is known
for example that coordination of Si atoms changes from $\sim 6.5$ in liquid silicon\cite{79} to $\sim 4$ in the amorphous phase. Moreover this approach can be readily applied to amorphous solids containing more chemical species, e.g. a-SiC:H or a-SiN:H.

4.2 Preparation of structural models

In the beginning the silicon atoms are placed in the diamond lattice sites with hydrogen atoms in interstitial positions. Next the cell is heated from 300 K to 2370 K, by velocity rescaling on each MD step. We set the time step to 1 fs. The initial velocities of the atoms are drawn randomly from the Maxwell-Boltzmann’s distribution. At 2370 K, when the system is completely melted, we let it evolve for 4 ps to destroy any trace of crystallinity. The cooling procedure takes $\sim 50$ ps to complete. In the temperature range 1818 K to 783 K we utilize a cooling rate of 0.023 K/fs, outside this range faster rates are used.

We have prepared a total of five different samples containing 64 silicon and 8 hydrogen atoms. We will denote these samples with letters A, B, C, D, and E. The supercells are cubic with a side of 11.062 Å. In order to check whether this size of models is sufficient we have performed a calculation on a bigger cell with 216 silicon and 27 hydrogen atoms. The side of the big cell is 16.593 Å. For both model sizes we use the experimental density of 2.2 g/cm$^3$.

4.3 Technical details

All calculations are performed with the Vienna Ab initio Simulation Package (VASP).\cite{40,41} The total energy and forces are calculated within the Generalized Gradient Approximation (GGA).\cite{57} Electron-ion interactions are described using the projector augmented wave method (PAW).\cite{42,74} We use standard PAW potentials distributed with the VASP package. The kinetic energy cutoff is set to 200 eV. During the whole MD run and the relaxation, we use only the $\Gamma$ point for Brillouin zone sampling. The partial occupancies are determined by the Methfessel-Paxton method\cite{75} with a smearing width of 0.2 eV. For calculations on the relaxed structures we use a $5 \times 5 \times 5$ Monkhorst-Pack mesh\cite{76} for the Brillouin Zone sampling and a Gaussian broadening of 0.05 eV.
Figure 4.1: Calculated (black line) and experimental\textsuperscript{45} (red line) partial pair-distribution functions. Both curves refer to systems at 300 K. The calculated curves are averages over five small samples.

4.4 Structural and electronic properties

A standard way of comparing the structure of models of amorphous solids to experiment is by using pair-distribution functions $g(r)$. In a binary compound there are three partial distribution functions for Si–Si, Si–H and H–H pairs. $g_{\alpha\beta}(r)$ gives the probability of finding atoms of type $\alpha$ and $\beta$ at a distance $r$ apart in a solid, relative to the case of an ideal gas (i.e. atoms distributed randomly in space). The overall agreement between the calculated and measured $g_{\text{Si-Si}}(r)$ and $g_{\text{Si-H}}(r)$ is good (see Fig. 4.1). We do not show the H–H functions because of the limited statistics. The main discrepancy that one notices immediately is that the calculated peaks are sharper than experimental ones. We believe that this is due to the limited resolution of the measurement. Our experience is that when one compares experiments with increasing resolution the first peak in the $g_{\text{Si-Si}}(r)$ becomes sharper. We refer the reader to publications of Bellissent et al.,\textsuperscript{45} Fortner et al.,\textsuperscript{46} Kugler et al.,\textsuperscript{47} and Laaziri et al.\textsuperscript{48}

Both theoretical curves in Fig. 4.1 account for the quantum mechanical nature of the nuclei. For an explanation on how this can be implemented see Ref. 81,115. As expected the corrections for $g_{\text{Si-Si}}(r)$ are negligible due to the high mass of Si atoms. In the case of $g_{\text{Si-H}}(r)$, however the peak height is reduced to a third of its original size.

When comparing the pair-distribution function for the small and big samples we see an over-all agreement. The first and second peak positions and the deviations do not differ significantly. This facilitates the use of
Table 4.1: The number of coordination defects in models of a-Si:H.

<table>
<thead>
<tr>
<th>sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>big cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-fold coord. Si</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5-fold coord. Si</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2-fold coord. H</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

modest cell sizes (~10 Å) for a-Si:H.

The cooling from liquid approach was criticized for creating models with a defect concentration that is too high. A device quality a-Si:H contains about $10^{16}$ defects per cm³. That means that there are about $10^6$ defect free Si atoms to one defect. Thus cells containing 100 atoms should be essentially defect free. In Table 4.1 we give an overview of defects present in our models. The models contain 3-fold coordinated Si atoms (dangling bonds) and 5-fold coordinated Si atoms (floating bonds). In addition the big cell contains a pair of 2-fold coordinated H atoms. As can be seen from the above, we define a defect as an atom that departs from its normal coordination. Thus all silicon atoms that are not 4-fold coordinated and all hydrogen atoms that are not 1-fold coordinated are considered to be defects. Two atoms are considered as bonded when they are closer than a certain cut-off distance. The Si–Si cut-off distance is 2.76 Å and the Si–H cut-off distance is 1.79 Å. These values correspond to the position of the first minima in the Si–Si and Si–H pair-distribution functions. We find that by using a cooling rate of 0.023 K/fs it is possible to prepare defect-free models of a-Si:H. It is likely that slower cooling rates have to be used to prepare defect free samples with a larger size.

In Fig. 4.2 we show the calculated density of states (DOS) for the defect-free samples A and C. They have a clean gap that is bigger than that of crystalline silicon. Samples B, D and E contain in-gap states with wave-functions localized on the defect atoms. The average band gap of small samples is 0.92 eV with a deviation of 0.10 eV. The gap of the big sample is 0.90 eV. Note that DFT underestimates semiconductor band gaps in general. However, as it is the case for experimental values, the calculated band gap of a-Si:H is larger than that of crystalline silicon. The width of in-gap states in the small cells is approximately 0.2 eV. This indicates that there is still a non-negligible interaction between the defects in neighboring cells.
4.5 The dangling bond defect

The dangling bond (DB) is believed to be the major defect in a-Si:H. Numerous experiments interpret the DB as the microscopic origin of the electron spin resonance (ESR) signal.\textsuperscript{116} According to the defect-pool model, the defect states in the band gap of a-Si:H originate from DBs in three charge states, i.e. negative, neutral and positive.\textsuperscript{117} Still several details about the DB defect are a subject of debate, e.g. the value of the formation energy and the size and sign of the correlation energy $U$.\footnote{The term “correlation energy” is misleading, since $U$ contains also other contributions. It is, however, widely used in literature on defects.}

We use our big cell of a-Si:H as a basis for preparing models of DBs. Originally it contains one DB and two interstitial H atoms (see Table 4.1). We remove the above mentioned defects by adding 3 H atoms. After relaxation the cell contains no structural defects and the DOS contains no in-gap states. Moreover, we anneal the structure at 300 K for about 1 ps, but find no changes in coordination or DOS.

It is important to prepare a larger number of models of DBs, since the disorder in a-Si:H can lead to considerable variation in formation energies. To account for this, we prepared 28 different models of a DB by

Figure 4.2: Calculated density of states of sample A (gray line), sample C (red line) and c-Si (black line). Because the sample contains 72 atoms only, the number of states is limited, and they can be seen as separate peaks. Each state appears as a broadened peak. The (artificial) interaction with the periodic images gives rise to a band-broadening.
Figure 4.3: Dangling bond in the negative, neutral and positive charge states (from left to right). Surfaces of the charge density with a constant value of 0.02 electrons/Å$^3$ are shown in red.

removing one hydrogen atom at a time (the other two hydrogen atoms form a molecule). There are strong indications that DBs exist in three charge states: as positive, neutral and negative. Thus after removing the H atom we charge the cell by adding or removing one electron, in the case of neutral DB the number of electrons remains unaltered. Next the structures are relaxed so that forces are smaller than 0.01 eV/Å. In Fig. 4.3 we show the atomic structure of a particular DB along with the charge density corresponding to its in-gap state.

The formation energy $E_{\text{form}}^q$ of a DB in a specific charge state $q$ is defined as follows:

$$E_{\text{form}}^q = E_{\text{def}}^q - E_{\text{bulk}}^q + E_H + q(E_f + E_{\text{val}} + \Delta V), \quad (4.1)$$

where $E_{\text{def}}^q$ and $E_{\text{bulk}}^q$ is the total energy of the cell containing the defect and a defect-free cell respectively. $E_H$ is the total energy of an isolated hydrogen atom. The Fermi energy $E_f$ is set to zero at the valence band maximum $E_{\text{val}}$ (in bulk material). The correction term $\Delta V$ is used to align electrostatic potential in the cells containing a DB and the defect-free cell. Values of the potential are taken from atoms far away from the defect to simulate a bulk-like environment.

In Figure 4.4 we show the formation energy as a function of Fermi level position for a particular DB. The three different lines correspond to different charge states. The slope of the lines indicate the charge state, e.g., positive slope corresponds to the positively charged DB, as follows directly from Eq. 4.1. Thermodynamic transition level $\epsilon(q_1/q_2)$ is defined as a Fermi level position where the charge states $q_1$ and $q_2$ have the same formation energy. Correlation energy $U$ is the difference between transition levels $\epsilon(0/-)$ and $\epsilon(0/+).$ Thus the DB depicted in Fig. 4.4 is a positive
U defect. If $U$ is negative, the neutral line lies above the point where the positive and negative lines cross. This type of defects will be always in a charged state, provided that, the neutral state is higher in energy by several $k_B T$.

We find that the formation energies of positive DBs have a considerable spread of 0.27 eV, the spread is smaller for the neutral and negative DB (0.17 and 0.14 eV respectively). The defect pool model uses a $U$ value of 0.2 eV. Our calculations show that there is a whole range of $U$ values, with an average of 0.13 eV and a standard deviation of 0.21 eV. We find that DBs can have also a negative $U$ (four cases) or a $U$ close to zero (two cases).

On three occasions it happened that after relaxation the DB and a nearby hydrogen atom reacted to form a hydrogen interstitial. Note that we discard this DB models and do not use them in our averages.

4.6 Conclusions

The cooling from liquid approach generates realistic models of a-Si:H that compare well to neutron scattering experiments. The use of rather modest cells (11.062 Å) is justified since we do not observe a significant change in the pair-distributions when increasing the cell size. On the other hand
the width of the defect states is 0.2 eV, what points to a non-negligible interaction between states in neighboring cells. For the first time we were able to prepare defect-free models with this method. We find three types of defects namely: 3-fold coordinated Si atoms (dangling bonds), 5-fold coordinated Si (floating bonds) and a 2-fold coordinated H atom. In the last part of the chapter we focus on the DB defect. We find that on average it is a positive $U$ defect with a $U$ of 0.13 eV. Interestingly we find that DB can be both a positive and negative $U$ defect.
Hydrogenated amorphous silicon nitride

5.1 Introduction

Hydrogenated amorphous silicon nitride (a-SiN$_x$:H) is a widely used dielectric material in the microelectronic industry. Its functions range from a passivation layer and selective etching mask to gate dielectric in thin film transistors (TFT). Device applications include TFTs for liquid crystal displays, nonvolatile semiconductor memory and a novel type of light emitting diode. The rapidly growing photovoltaic industry utilizes thin films of a-SiN$_x$:H to minimize reflection losses of solar cells.

Thin films of silicon nitride are deposited using different types of chemical vapor deposition (CVD) and sputtering. The material is non-stoichiometric in general and contains considerable amounts of hydrogen depending on the preparation conditions.

Along with the experimental interest in a-SiN$_x$:H, several theoretical studies have been performed. In general the studies consist of two consecutive parts. First one needs to obtain a structural model of the amorphous network. Next the electronic and vibrational properties can be analyzed. The preparation of structural models can be roughly divided into two approaches:

The first one is based on cooling from a liquid to room temperature. When the cooling rate is high enough, the system does not have time to crystallize and it ends up in a metastable (amorphous) state. The process of cooling is simulated either by molecular dynamics (MD) or Monte
Carlo calculations. The interaction between atoms can be described either by a force field (inter-atomic potentials)\textsuperscript{127–132} or with \textit{ab-initio} methods. The force field calculations enable one to evolve relatively big systems for longer periods of time.\textsuperscript{133–136} On the other hand the transition from liquid to solid poses difficult requirements on the inter-atomic potentials, since the potential has to describe the liquid and solid phase accurately at the same time. In the case of silicon, for example, the coordination changes from $\sim6$ to 4 and the system additionally undergoes a metal to semiconductor transition.\textsuperscript{143} Quantum mechanical calculations (mostly based on the Density Functional Theory \textit{[DFT]}) provide a realistic description of the chemistry and bonding of the system but are restricted to smaller system sizes and shorter simulation times.\textsuperscript{137–140}

The second approach to preparation of amorphous structures is based on an \textit{a priori} assumption about a certain property of the network. We could, for example, require that all Si and N atoms are 4-fold and 3-fold coordinated respectively or that the network is chemically ordered (there are no Si–Si and no N–N bonds). A classical example of such a method is the bond switching algorithm by Wooten et al.\textsuperscript{63} applied to a-Si. It was recently extended by Kroll\textsuperscript{141} to generate samples of a-Si$_3$N$_4$.\textsuperscript{142} Ouyang and Ching randomly combined six types of subunits to obtain a continuous random network model of a-Si$_3$N$_4$ with the correct topology.\textsuperscript{144}

A majority of the above studies are on pure stoichiometric silicon nitride. Calculations on hydrogenated material are more rare\textsuperscript{132,141,142,145} and so far no entirely \textit{first principles} calculation has been performed. Depending on the Plasma Enhanced CVD deposition conditions very different materials can be prepared: Giorgis et al. deposited a material with density 2.0 g/cm$^3$ containing 30 at.% of hydrogen.\textsuperscript{125} A much more dense material is deposited when the feedstock gasses are diluted with hydrogen. This results in a material with density 3.0 g/cm$^3$ and 18 at.% of hydrogen.\textsuperscript{125} Interestingly the Hot Wire CVD technique also yields high-density films with a similar composition.\textsuperscript{126}

In this study we investigate a-SiN$_x$:H with equal amounts of silicon and nitrogen ($x=1$). Our motivation is to understand the structure and electronic properties of nitrides other than stoichiometric. We have prepared models for both low and high density phases of a-SiN:H utilizing the above mentioned experimental compositions. The models of the amorphous network are prepared with the “cooling from liquid” method, that was successfully applied previously to study a-Si:H.\textsuperscript{115,146} We analyze the
short range order and report on the coordination of atoms, the mean and
deviation of the bond lengths. The possibility of void creation and phase
separation at two very different densities is investigated. Defects, acting
as trapping sites, can dramatically influence the transport properties of a
material. We report both on Si- and N-based defects that are under- or
over-coordinated. The electronic structure of the nitrides is analyzed. The
character of the valence and conduction bands explains the relationship
between the band gap size and the nitride composition. The preparation
of amorphous structures with the cooling from liquid method is arbitrary
to some extend. Two major factors that affect the quality of the models
are the cell size and the cooling rate used. We estimate these effects by
comparing models prepared under different conditions.

The chapter is organized as follows. Section 5.2 describes settings used
during the calculations. The generation of the structural models is de-
scribed in Sec 5.3. Section 5.4 contains three subsections devoted to:
structure at short range, structure at long range, defects and electronic
properties. A discussion of the cell size and cooling rate effects is pre-
sented in Sec. 5.5 and 5.6. Our main findings are summarized in Sec. 5.7.

5.2 Technical details

The total energy and forces are calculated within DFT using the General-
ized Gradient Approximation (GGA). All calculations were performed
with the Vienna Ab initio Simulation Package (VASP). Electron-ion
interactions are described using the projector augmented wave method. MD calculations were performed with a “soft” nitrogen potential and a
250 eV kinetic energy cut-off. For static calculations a 400 eV cut-off and
“normal” potentials supplied with VASP were used. The performance of
the potentials was tested on α and β phases of Si₃N₄. The calculated cell
parameters were higher than experimental ones by less than 1 %. The
difference in cell parameters between the “soft” and “normal” potential
was less than 0.1 %. During the whole MD run and the relaxation, we
use only the Γ point for Brillouin zone sampling. When calculating the
density of states of the relaxed structures the Brillouin zone is sampled
with a 3×3×3 and a 5×5×5 Monkhorst-Pack mesh for the “big” and
“small” cells (for an explanation, see below) respectively. In both cases a
Gaussian smearing with a width of 0.05 eV is used. Molecular dynamics
calculations were performed with a 1 fs time step.
5.3 Preparation of the structure

The amorphous structures are prepared by the cooling from liquid approach. At first atoms are placed randomly in the supercell at distances larger than the sum of their covalent radii. This prevents large forces at the start of the MD calculation. The velocities of the atoms are initialized according to the Maxwell-Boltzmann distribution such that the temperature of the system is 300 K. Next the system is heated to 3060 K with a constant rate of 1.38 K/fs. The temperature is controlled by velocity rescaling at each MD step. At 3060 K the system is a liquid, with the root mean squared displacement growing linearly in time. The density of states has a depression around the Fermi energy, however no band gap is formed. The liquid is equilibrated for 8 ps at this temperature. Next the sample is cooled back to room temperature. We utilize two different cooling rates: 1.380 K/fs and 0.023 K/fs (see Fig. 5.1). We will refer to them as the fast and the slow cooling rate. After reaching 300 K the samples are evolved for another 0.5 ps to calculate the structural averages. Next the structures are relaxed in order to calculate the electronic properties.

The low density cell $\text{Si}_{128}\text{N}_{128}\text{H}_{114}$ is cubic with a side of 16.59 Å. The high density cell $\text{Si}_{194}\text{N}_{194}\text{H}_{85}$, containing much less hydrogen, has the same dimensions. Both were prepared with the slow cooling rate and we will refer to them as “big” cells. Additionally, we have prepared four “small” cells $\text{Si}_{38}\text{N}_{38}\text{H}_{34}$ with dimensions $11.06 \, \text{Å} \times 11.06 \, \text{Å} \times 11.09 \, \text{Å}. 

Figure 5.1: Thermal procedure used to prepare amorphous structures of a-SiN:H. The three slow quench samples are marked with letters A, B and C.
These cells contain low density nitride. One was prepared with the fast cooling rate and three with the slow cooling rate. The compositions and densities are based on measurements by Giorgis et al. Unless stated otherwise, below we report data on the big cells only.

5.4 Low and high density phases of a-SiN:H

5.4.1 Structure at short range

Although amorphous silicon nitride lacks the long range order of a crystal, the strong covalent bonding orders the atoms at shorter distances. This short range order is to some extent similar to the crystalline α and β stoichiometric phases, where Si atoms are bonded to 4 N atoms with bonds defining a tetrahedral angle of 109° and N atoms bonded to 3 Si atoms in a planar configuration with angles of 120°. Indeed the bond angle distributions of a-Si₃N₄ reported by Giacomazzi and Umari have means close to the above values. The distributions are however considerably broadened. Since the material under study is silicon rich and contains a considerable amount of hydrogen there are also differences.

In order to characterize the short range order in amorphous solids pair-distribution functions $g(r)$ are routinely employed. These give the probability of finding two atoms at a distance $r$ apart in the system under study, normalized by this probability for a completely disordered system at the same density. Since our samples contain three different chemical elements there is a total of six partial distributions. In Figure 5.2 we plot only partial distributions that do not contain hydrogen. In both the low and high density phases the Si–Si pair-distribution has two prominent peaks. The first peak gives a hint that the material is non-stoichiometric. It is mostly due to Si–Si bonds, but also contains a small contribution from silicon atoms that form square shaped structures. These “square structures” are formed by two silicon atoms in opposite corners of a square along with two nitrogen atoms placed in the remaining corners. The structure is planar with angles close to 90°. Similar structures were observed before in theoretical models of a-Si₃N₄. Kroll reports on four-membered rings, that induce peaks at 90° in the bond angle distributions. Giacomazzi and Umari describe the very same structure as “edge-sharing tetrahedra”. The second peak in $g_{Si-Si}$ is formed by silicon atoms that are connected to a common nitrogen atom. The first peak of $g_{N-N}$ has a shoulder due to nitrogen atoms that form the “square structures”. Nitrogen atoms bonded
Figure 5.2: Partial pair-distributions of big cells: Si–Si (upper part), Si–N (middle part) and N–N (lower part). The black solid and red dashed lines correspond to the low and high density nitride respectively. All curves refer to systems at 300 K.
to a common silicon atom contribute to the first main peak. Note that there are no N–N bonds present in the samples and thus the corresponding peak is missing. The Si–H and N–H pair-distributions (not shown) have well-defined and sharp first peaks that are due to hydrogen bonded to silicon or nitrogen atoms respectively. The peak positions in $g_{Si-H}$ and $g_{H-N}$ correspond to calculated bond lengths in the SiH$_4$ and NH$_3$ molecules respectively. A similar amount of hydrogen molecules is formed in both samples: 16 and 10 for low and high density nitride respectively.*

Examining the structure of the low density nitride, we find that it has a very open structure with void space that forms a percolating network. The internal surface of the void-like structure accommodates most of the hydrogens who bind to Si and N. The H$_2$ molecules reside in the void space. The high density nitride contains 1.5 times more Si and N atoms in the same volume and thus has a much higher packing. We note that both crystalline phases have a density of 3.2 g/cm$^3$, comparable to the density of our high density material. Additionally to void space being filled up we find structural changes in the network.

As can be seen in Fig. 5.2 all peaks in the pair-distributions have a smaller intensity in the high density nitride, indicating that it is more disordered. As a general trend we find that bonds in the high density nitride are compressed as compared to the low density phase (see Table 5.1). The first peak in the $g_{Si-Si}$ distribution shifts from 2.41 Å to 2.35 Å. The silicon-nitrogen bonds are more rigid and their length changes by only 0.01 Å. The second neighbor distances in the $g_{Si-Si}$ and $g_{N-N}$ shift to smaller distances as well. This implies that the average angles centered at the nitrogen and silicon atoms respectively, are smaller in the high density nitride. The change in the geometry of the square structures is small. The Si-Si and the N-N distances are compressed by 0.01 Å and 0.02 Å respectively in the dense nitride. Surprisingly, in the cell with a higher atomic density there are only 8 “square structures” compared to the low density cell which contains 14 of the structures. The fluctuation in these values could be deduced from the small cells, where the deviation in the number of “square structures” is around 1 (see Tab. 5.3). It is not expected that the structures are remnants of the liquid phase, because their concentration is lower at higher temperatures.

*Under the assumption that H$_2$ molecules are not incorporated into the films during the deposition, the actual concentration of hydrogen in our cells would change. The low and high density cell would contain 24 and 14 at. % of hydrogen respectively. Expected changes in density are small due to the small hydrogen mass.
Table 5.1: Peak position $r$ and width $\sigma$ (or standard deviation of the distance) in pair-distribution functions not containing hydrogen. Superscripts indicate either the first or second peak. All values were obtained from relaxed structures and thus refer to systems at 0 K. Values are in Å.

<table>
<thead>
<tr>
<th>cell</th>
<th>$r_{\text{Si-Si}}$</th>
<th>$r_{\text{Si-Si}}$</th>
<th>$r_{\text{Si-N}}$</th>
<th>$r_{\text{N-N}}$</th>
<th>$\sigma_{\text{Si-Si}}^1$</th>
<th>$\sigma_{\text{Si-Si}}^2$</th>
<th>$\sigma_{\text{Si-N}}^1$</th>
<th>$\sigma_{\text{N-N}}^1$</th>
</tr>
</thead>
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<tr>
<td>fast</td>
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<td>3.084</td>
<td>1.753</td>
<td>2.904</td>
<td>0.071</td>
<td>0.178</td>
<td>0.050</td>
<td>0.143</td>
</tr>
<tr>
<td>slow A</td>
<td>2.449</td>
<td>3.080</td>
<td>1.765</td>
<td>2.912</td>
<td>0.097</td>
<td>0.161</td>
<td>0.033</td>
<td>0.144</td>
</tr>
<tr>
<td>slow B</td>
<td>2.415</td>
<td>3.081</td>
<td>1.756</td>
<td>2.913</td>
<td>0.089</td>
<td>0.162</td>
<td>0.029</td>
<td>0.142</td>
</tr>
<tr>
<td>slow C</td>
<td>2.416</td>
<td>3.038</td>
<td>1.756</td>
<td>2.924</td>
<td>0.066</td>
<td>0.145</td>
<td>0.032</td>
<td>0.145</td>
</tr>
<tr>
<td>low</td>
<td>2.414</td>
<td>3.087</td>
<td>1.758</td>
<td>2.917</td>
<td>0.081</td>
<td>0.160</td>
<td>0.035</td>
<td>0.155</td>
</tr>
<tr>
<td>high</td>
<td>2.352</td>
<td>3.030</td>
<td>1.745</td>
<td>2.854</td>
<td>0.079</td>
<td>0.184</td>
<td>0.045</td>
<td>0.152</td>
</tr>
</tbody>
</table>

Table 5.2: Coordination of silicon and nitrogen atoms in the low and high density nitride. Artificial Si–Si bonds are discarded from the count.

<table>
<thead>
<tr>
<th>cell</th>
<th>Si by Si</th>
<th>Si by N</th>
<th>Si by H</th>
<th>Si by all</th>
</tr>
</thead>
<tbody>
<tr>
<td>low dens.</td>
<td>0.84</td>
<td>2.68</td>
<td>0.45</td>
<td>3.98</td>
</tr>
<tr>
<td>high dens.</td>
<td>0.88</td>
<td>2.90</td>
<td>0.26</td>
<td>4.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>cell</th>
<th>N by Si</th>
<th>N by N</th>
<th>N by H</th>
<th>N by all</th>
</tr>
</thead>
<tbody>
<tr>
<td>low dens.</td>
<td>2.68</td>
<td>–</td>
<td>0.30</td>
<td>2.98</td>
</tr>
<tr>
<td>high dens.</td>
<td>2.90</td>
<td>–</td>
<td>0.13</td>
<td>3.03</td>
</tr>
</tbody>
</table>

In order to calculate coordination numbers, six cut-off distances need to be defined. The cut-off distances are chosen as the position of the minimum after the first peak in the corresponding partial pair-distribution. The exception to this rule is the N–N bond, since there are no such bonds present in our samples. The N–N cut-off distance is set approximately to the bond length of the $N_2$ molecule (1.20 Å). The minima in the Si–Si pair-distribution are different for the two samples. Hence we use also different cut-off distances for low and high density nitride (2.65 and 2.55 Å respectively). For the Si–N pair a cut-off distance of 2.00 Å is used. The Si–H and N–H cut-off distances are 1.65 Å and 1.15 Å respectively. Two H atoms are considered bonded when less than 0.85 Å apart.

In table 5.2 the coordination distributions of the low and high density nitride are listed. As expected, in both the low and the high density system the number of first neighbor is close to what is ideally expected, given the valence of the atoms: 3.98 and 4.04 for Si (low and high density nitride respectively) and 2.98 and 3.03 respectively. So there seems to be slight
tendency for under (over) coordination in the low (high) density nitride. The ratio of Si–H bonds to N–H bonds is 1.53 and 2.00 for the low and high density nitride respectively. Thus hydrogen atoms form bonds preferably to silicon at both densities.

### 5.4.2 Structure at longer length scales

To analyze the structure at intermediate and longer length scales and study how it copes with non-stoichiometry we discuss the structure factors that provide a more natural means. The Ashcroft-Langreth (AL) and Bhatia-Thornton (BT) structure factors are plotted in Fig. 5.3 and 5.4 respectively. Both sets of structure factors have been constructed only from silicon and nitrogen atoms, disregarding any hydrogen contributions. The partial structure factors $S_{nn}(q)$, $S_{ne}(q)$ and $S_{cc}(q)$ are Fourier transforms of the (real space) pair-distribution functions that describe correlations among number density and concentration fluctuations. A direct comparison with experiments is possible through the neutron structure factor in Fig. 5.5. Here the hydrogen atoms were included in the calculation. We have used scattering lengths of 4.1491, 9.36 and -3.739 fm for silicon, nitrogen and hydrogen respectively. Unfortunately neutron measurements are available only for stoichiometric and hydrogen free material, so we plot only the calculated curves.

In both the high and the low density nitride the $S_{cc}$ has a pronounced main peak at $q \approx 2.8 \text{ Å}^{-1}$. This corresponds to a real space distance of roughly $7.7/2.8 = 2.8 \text{ Å}$, which is close to the position of the main peak of $g_{NN}$ (2.9 Å) and only slightly further from the main peak in $g_{SiSi}$ (3.0-3.1 Å). Indeed it signals the concentration fluctuations that occur because of the main structural motif: the Si-N-Si and N-Si-N with quite rigid bond angles giving rise to homo-coordination at the corresponding length scale. The main peak in $S_{nn}$ occurs just below 5 Å$^{-1}$, roughly corresponding with a real space distance of 1.6 Å, quite close to the peak in $g_{SiN}$ (1.75 Å).

In the following we focus on the differences between the high and low density nitride. In the high density nitride a “prepeak” in $S_{nn}$ occurs almost at the same $q$ as the main peak in $S_{cc}$, i.e. around $q = 2.5 \text{ Å}^{-1}$. The peak in $S_{nn}$, however, is much broader than the sharp peak in $S_{cc}$. Moreover, it is shifted towards smaller wave-vectors. Evidently the number density fluctuations occur at slightly longer and less sharply defined distances as the concentration fluctuations. This peak coincides with a similarly shaped peak in $S_{SiSi}$ suggesting that it originates from fluctua-
Figure 5.3: Calculated Ashcroft-Langreth structure factors of the low density (black solid line) and high density (red dashed line) nitride. Structure factors are averages over 500 MD steps (at 300 K) and were calculated for the big cells.
Figure 5.4: Calculated Bhatia-Thornton structure factors of the low density (black solid line) and high density (red dashed line) nitride. Structure factors are averages over 500 MD steps (at 300 K) and were calculated for the big cells.
Figure 5.5: Calculated neutron structure factors of the low density (black line) and high density (red line) nitride. Structure factors are averages over 500 MD steps (at 300 K) and were calculated for the big cells.

...tions in the Si number density. These fluctuations might be a way how the system tries to cope with the non-stoichiometry, but such a conclusion remains speculative. Indeed we do not know the $S_{cc}$ of the stoichiometric silicon nitride, but its neutron structure factor has a small hump at $q \approx 2.0 \text{ Å}^{-1}$, just before the large peak at $q = 2.8 \text{ Å}^{-1}$. At the longest wavelengths that we can access in our small cells, we observe a considerable increase in $S_{NN}$ again, but not in $S_{SiSi}$. Evidently the dense nitride tries to deal with the non-stoichiometry by creating nitrogen rich and nitrogen poor regions, showing some tendency to phase separation. Concomitantly the $S_{cc}$ shows a small upward bend for $q \to 0$.

Now let us consider the low density nitride. Where in the high density nitride only $S_{NN}$ shows an appreciable increase for $q \to 0$, here all three AL partials have considerable values in this limit. Turning towards the BT structure factors, we see this translated in all of them. $S_{cc}$ is very similar to the high density $S_{cc}$ over the whole $q$ range in Fig. 5.4. In the low $q$ range it has a small peak near 0.6 Å$^{-1}$ that signals large scale composition fluctuations. On the other hand there is a downturn for the minimal $q$ value that prevents an unambiguous conclusion about the phase separation. Additionally, the statistical noise is large for these small $q$ values. The most striking effect is observed for $S_{nn}$. For large $q$ values it traces the high density $S_{nn}$ rather closely, but it does not have a prepeak near $q = 2.5 \text{ Å}^{-1}$, and moreover retains a large amplitude for all $q$ in the long wave length...
Table 5.3: A summary of defects present in different samples. Artificial Si-Si bonds inside “square structures” are discarded from the count. The number of the structures is listed in the first column. S2 denotes a 2-fold coordinated silicon atom. Column denoted by $D_{str}$ contains total counts of structural defects. Column $D_{elc}$ gives the integrated DOS inside the band gap. The last column contains cohesive energies of cells per Si atom in eV.

<table>
<thead>
<tr>
<th>cell</th>
<th>sq</th>
<th>Si2</th>
<th>Si3</th>
<th>Si5</th>
<th>H0</th>
<th>N2</th>
<th>N4</th>
<th>$D_{str}$</th>
<th>$D_{elc}$</th>
<th>$E_{coh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast</td>
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<td>5</td>
<td>2</td>
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<td>2</td>
<td>1</td>
<td>10</td>
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<tr>
<td>slow A</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>13.13</td>
</tr>
<tr>
<td>slow B</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>13.19</td>
</tr>
<tr>
<td>slow C</td>
<td>6</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>13.15</td>
</tr>
<tr>
<td>low dens.</td>
<td>14</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>0</td>
<td>13</td>
<td>12</td>
<td>13.17</td>
</tr>
<tr>
<td>high dens.</td>
<td>8</td>
<td>0</td>
<td>5</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>22</td>
<td>14</td>
<td>—</td>
</tr>
</tbody>
</table>

limit. This is a clear signature of the void formation, which exposes a large internal surface area that is covered with saturating hydrogen atoms. Thus, for the low density nitride, we observe long wavelength composition fluctuations, but more importantly, we also see density fluctuations coming from the void formation.

5.4.3 Defects and electronic properties

The notion of a defect in an amorphous solid is linked to the coordination of an atom. Atoms that deviate from the proper coordination (Si 4-fold, N 3-fold and H 1-fold) are considered to be defects. Previously we have defined cut-off distances that enable us to retrieve the coordination of an atom. It turns out, however, that here the cut-off criterion is a too simple one: The two silicon atoms making up the “square structure” are within the specified cut-off distance but are not bonded. These “bonds” are artificial and we account for this fact in the coordination and defect counts.

In Table 5.3 we give an overview of defects found in the low and high density nitride samples. In absolute values there are more defects in the high density nitride. When taking the number density into account the defect concentrations are similar. Interestingly there are 2.6 times more Si defects than N defects at both densities. The low density nitride favors under-coordinated defects, whereas the high density material favors over-coordinated defects.

In Figure 5.6 we show the calculated electronic density of states of the
Figure 5.6: Calculated electronic density of states of the low density (black solid line) and high density (red dashed line) nitride. Both curves are aligned with respect to the “center of mass” of occupied states (at 0 eV). The arrow marks the Fermi energy of both cells.

big cells. The DOS curves are aligned at the “center of mass” of occupied states. We find that throughout the low density cells the overall shape of the valence band, represented by the “center of mass” of occupied states, is similar. The variations are larger in the gap region. This method is thus more robust than aligning at the top of the valence band and will be used in the following discussion. From Figure 5.6 we see, that both models have a clearly defined band gap. The low density nitride has a gap of 2.2 eV. The band gap of the high density nitride is larger by 0.5 eV at a range of DOS levels. Note, that DFT underestimates semiconductor band gaps in general.

Next we calculate the site projected DOS, which enables us to split the total DOS into contributions from different chemical elements (see Fig. 5.7). We find that in the case of amorphous silicon nitride, the edges of the valence band extending from −3 eV to 7 eV are dominated by states localized at silicon atoms. The middle part of the band originates mostly from states located at nitrogen atoms. In the crystalline phases, that are stoichiometric, the situation is different. The lower part of the band is due to silicon and the upper part due to nitrogen. The conduction band is formed by silicon states in both cases. This finding is in agreement with measurements of the optical gap with varying composition of a-SiN$_x$:H. The band gap increases with increasing nitrogen content or decreasing
Figure 5.7: Relative contribution of silicon (red solid line), nitrogen (green dashed line) and hydrogen (blue dotted line) atoms to the total DOS. The case of high density nitride and $\alpha$-Si$_3$N$_4$ is shown in the top and bottom panel respectively. Horizontal bars mark the band gap region. All curves are aligned with respect to the “center of mass” of occupied states (at 0 eV).
number of Si–Si bonds.\textsuperscript{125,151}

All of the samples except sample B contain a number of in-gap electronic defect states. In the following we will compare the amount of structural and electronic defects using two approaches. In the first approach, we integrate the density of states inside the gap. The range of integration (band gap edges) depends on the density and is indicated in Fig. 5.8. In the low density nitride the amount of defect states obtained in this way is comparable with the number of structural defects (see Table 5.3). The agreement is worse for the dense nitride. In the second approach, we again make use of the site projected DOS. This time, however, we sum over atoms that are structural defects. As can be seen from Fig. 5.8 the major contribution to in-gap states comes from silicon atoms. Note, that the sum over the structural defects does not add up to the total DOS inside the gap regions. From this follows that the in-gap states have contributions from non-defective atoms. Additionally, there are structural defects that do not contribute to in-gap states. The ratio of electronically active defects is one half in the small cells, and decreases to one third in big cells. Thus, in our models, we do not observe a one-to-one correspondence between structural and electronic defects.

5.5 Effects of the cell size

First-principles methods, being more computationally intensive, are restricted to smaller system sizes. Here we investigate how the properties of the amorphous network change when comparing the small and big cells prepared with the slow cooling rate. Only cells containing low density nitride are used for this purpose.

As can be seen in Fig. 5.9 there are no statistically significant effects on the pair-distributions by the cell size. The peak positions and widths are similar in the small and big cells. The biggest discrepancy is in the second peak of $g_{\text{Si–Si}}$, which for the small cells is shifted to lower values by 0.02 Å (see Table 5.1). For both cell sizes the silicon atoms show a tendency to under-coordination. There are also more under- than over-coordinated defects. The same trend holds for nitrogen atoms, with an average under-coordination and more under-coordinated defective nitrogens. The ratio of Si-H to N-H bonds is 1.41 and 1.53 for the small and big cells respectively. The cohesive energies per Si atom are similar for different cell sizes (see Table 5.3). The only parameter that stands out
Figure 5.8: Density of states due to structural defects of the low (top panel) and high (bottom panel) density nitride. Contributions from silicon and nitrogen defect atoms are shown in red and green respectively. The total projected DOS, summed over all atoms, is in black. The horizontal bars mark the band gaps. All curves are aligned with respect to the “center of mass” of occupied states (at 0 eV).
Figure 5.9: Comparison of pair-distributions of the small cells prepared by slow cooling (gray), small cell prepared by fast cooling (red solid line) and the big low density cell prepared by slow cooling (green dashed line). The gray area extends from the minimum to the maximum values determined from the distributions of samples A, B and C. Only partial distributions not containing hydrogen are shown: Si–Si (upper part), Si–N (middle part) and N–N (lower part). All curves refer to systems at 300 K.
in the comparison is the number of defects (see Table 5.3). If we would merge the three small samples they would have 4 defects out of 330 atoms. The big cell, containing 13 defects out of 370 atoms, has quite a higher defect concentration. A possible explanation for this behavior would be that bigger cells, having more degrees of freedom, result in an increased defect formation.

5.6 Cooling rate effects

The preparation of models of amorphous solids by cooling from the liquid is arbitrary to some extent. It does not mimic the experimental process. Cooling rates that are too high will result in structures with an excess of disorder. In previous studies, Alvarez et al. quenched samples that were heated just below the melting temperature with a rate of 3.1 K/fs.\textsuperscript{138,139} Giacomazzi et al. cooled their sample from 3500 K to 2000 K, using a rate of 0.3 K/fs.\textsuperscript{140} Both authors studied pure silicon nitride. In this section we attempt to assess the effect of the cooling rate on the amorphous network.

Figure 5.9 shows the comparison of the small cells prepared by fast and slow cooling rate. The biggest effects are again in the Si–Si partial distribution. The positions of the first and second peak do not change significantly. The disorder in the “fast” cell is rather manifested by larger variations in the second neighbor distances (0.178 Å for the Si–Si pair), that are proportional to deviations in bond angles. The number of “square structures” is comparable, however there are much more Si–Si bonds in the sample prepared by the fast rate. The faster cooling rate also seems to result in more variation in the Si–N bond length. After a fast quench the cell contains a large number of hydrogen molecules and defective 3-fold coordinated silicon atoms. When using a slower cooling the hydrogen gets incorporated into the network more effectively, passivating under-coordinated defects. The bonding of hydrogen to nitrogen is mostly unaffected.

As mentioned above a sizable difference between the cells is the number of defects they contain. With the use of the slow cooling rate, we were in fact able to prepare a defect free structure (sample B). Cells containing hundreds of atoms should be defect free in order to be comparable with the real device quality material. In the past, with very short simulation times, this has however proven to be difficult to achieve. Table 5.3 summarizes the number of defects for different cooling rates discarding any artificial bonds from the count. The fast quench cell, being more disordered has also
the lowest cohesive energy among all the slow quench cells (see Table 5.3).

5.7 Conclusions

Atomistic models of hydrogenated amorphous silicon nitride (a-SiN:H) with equal amounts of silicon and nitrogen were prepared for two very different densities; 2.0 g/cm$^3$ and 3.0 g/cm$^3$. The short range order is to some extent similar to the crystalline $\alpha$ and $\beta$ stoichiometric phases. Silicon atoms are mostly 4-fold coordinated forming a tetrahedral unit. Nitrogen atoms are mostly 3-fold coordinated with bonds lying in a plane. Since the material under study is silicon rich and contains a considerable amount of hydrogen there are also differences. We find Si–Si bonds (but no N–N bonds). There are “square structures” consisting of 2 Si and 2 N atoms positioned in opposite corners of a square. The low density nitride has a very open structure with void space that is largely connected into a percolating network. The internal surface accommodates the covalently attached hydrogens. When the density is increased this void space is filled up. Moreover, bonds get compressed, bond angles get smaller and the average coordination increases. At both densities the ratio of Si–H to N–H bonds is larger than 4/3 indicating the preference of hydrogen to bind to silicon.

Interestingly, the analysis of the structure at longer range revealed some tendency for the high density nitride to phase separate. The Bhatia-Thornton structure factors show that nitrogen rich and nitrogen poor regions are formed (this is very hard to see just from plots of the 3D structure, as only few atoms are involved). In the low density nitride long wavelength composition fluctuations also occur, but a tendency to phase segregation is less evident. In contrast with the high density material, here we observe the formation of void space, that is confirmed by the calculated structure factors. We note that the low density nitride has a 1.5 times smaller density and a $\sim$1.3 times higher hydrogen concentration compared to the dense nitride.

In the second part of the chapter we investigate coordination defects and electronic properties of a-SiN:H. We find that at both densities there are more Si defects than N defects. The high density phase has a higher defect concentration because of the higher number density. The high density nitride favors over-coordinated defects, while the low-density phase favors under- coordinated defects. We have calculated the density of states for
both phases and find a DFT gap of 2.2 eV and 1.7 eV for the low and high density nitride respectively. The density of states at the band gap edges is dominated by states localized at silicon atoms. Decreasing silicon content opens up the gap, which is consistent with experimental knowledge. We find that less than half of the structural defects are electronically active. In the low density nitride, integrating the DOS in the gap region gives values close to the number of structural defects. This approach is not universal and fails for the dense nitride.

In the final part of the chapter we investigate whether the small cell systems are more affected by the constraints by the periodic boundary conditions, but we do not find any statistically significant differences, except for the number of defect states. We also try to estimate the effect of the cooling rate on the amorphous network. The samples prepared by fast cooling seem to be more disordered, with larger bond angle deviations, more defects and a higher cohesive energy. Using a rate of \( \sim 0.02 \text{ K/fs} \) we succeeded in preparing a defect free structure containing \( \sim 100 \) atoms.
Chapter 6

Quantum confinement and band offsets in the a-Si:H/a-SiN:H multilayer

6.1 Introduction

Multilayers (ML), consisting of alternating layers of two semiconductors with different band gaps, belong to the group of man-made materials. Layers with smaller and bigger band gaps are referred to as “well” and “barrier” respectively. The thickness of the well layer is in the nanometer range resulting in the confinement of charge carriers. By changing the thickness of the well one can tune the band gap of the multilayer. Using this elegant approach optoelectronic devices, deposited over large areas and on cheap substrates, could be fabricated. These include light-emitting devices\textsuperscript{152,153} and solar cells.\textsuperscript{154,155}

A considerable part of the experience with ML structures comes from crystalline semiconductors. The two materials have to be lattice matched in order to grow epitaxially on top of each other. In order to remove this restriction, Abeles and Tiedje fabricated a ML from amorphous semiconductors.\textsuperscript{25} Reports on the increase of the optical gap,\textsuperscript{25–27,29–31} resonant tunneling\textsuperscript{27,28} and the shift of the photo-luminescence peak followed.\textsuperscript{32,33} The observed effects were attributed to quantum confinement of charge carriers, often employing the quantum well model to fit the data. The existence and magnitude of quantum effects in amorphous / amorphous nanostructures is, however, still debated. Collins and Huang claim that
the use of the Tauc law can introduce systematic errors in optical gaps when used on multilayers.\textsuperscript{34} Beaudoin et al. observe the usual confinement effects for the Tauc gap, but not for the Cody gap.\textsuperscript{36} Steps in the current-voltage characteristics were attributed to other effects than to resonant tunneling.\textsuperscript{35,37} Reviews on the subject can be found in Bernhard et al.\textsuperscript{38} and Koehler.\textsuperscript{39}

In order to gain new insight into this problem, we have prepared an atomistic model of a hydrogenated amorphous silicon (a-Si:H) based multilayer. The barrier layer is composed of silicon nitride (a-SiN:H) used often in the above mentioned experiments. The atomistic model allows us to study quantum confinement effects directly without the need for transport or optical measurements. As argued above, the interpretation of such measurements could be complicated by interface effects or the inappropriate use of models to extract the optical band gap.

Since MLs are composed of a large number of layers, the interface between the two semiconductors is of importance. For a large part the knowledge about the a-Si:H/a-SiN:H interface comes from research on thin film transistors, where the nitride is used as a gate dielectric. At present these transistors are used in a commercial production of liquid crystal displays (LCDs).\textsuperscript{120,156} The current opinion on the interface structure differs between experimental groups. This is probably because of the flexibility of the amorphous materials allowing to fabricate different interfaces by changing the deposition conditions. Roxlo et al.\textsuperscript{157} report that the interface is atomically sharp, containing a broader disordered region with an excess hydrogen concentration of $10^{15}$ cm$^{-2}$. Defects can be created at both the silicon and nitride side of the interface. According to Roxlo et al. this depends on the order of deposition, because defects are created in the material that is being grown and not in the substrate material. Matsumoto et al. give an explanation why the silicon-on-nitride interface has superior electrical properties than the nitride-on-silicon interface. According to their investigation depositing nitride on silicon causes hydrogen effusion from silicon, leaving it with more defects.\textsuperscript{158} An in-situ study of Drevillon et al. offers a different explanation. They find that nitride-on-silicon interface is sharp while the silicon-on-nitride has a gradual change in composition.\textsuperscript{159} This leads to a more relaxed network and thus to a better electronic performance.

The investigation of amorphous MLs or amorphous/amorphous interfaces with atomistic models was limited so far, mostly due to the compu-
tational cost. Kuzuu et al.\textsuperscript{160} investigated the structure of the \(a\text{-SiO}_2/a\text{-SiO}_2\) interface. Several studies focus on interfaces of crystalline silicon with either pure amorphous silicon \(a\text{-Si}\)\textsuperscript{161–169} or glass \(a\text{-SiO}_2\).\textsuperscript{170–176} Only a part of these studies addresses also the band offsets between the materials.\textsuperscript{166,169–171,173,175,176} Calculations on the \(c\text{-Si}\) and hydrogenated amorphous silicon were performed by Tosolini et al. and Van de Walle et al.\textsuperscript{70,169} The preparation of structural models of the amorphous materials usually relies on interatomic potentials with the exception of Pasquarello et al.,\textsuperscript{174,176} who used first-principles molecular dynamics (MD).\textsuperscript{59} We also think that this level of accuracy is necessary to describe the various structural and chemical environments that can occur at the interface.

The chapter is organized as follows. Section 6.2 contains technical details of the calculation. Generation of atomistic models of the ML is described in Sec. 6.3. In Section 6.4 we characterize the structure of the interface in terms of density and concentration profiles. The magnitude of the quantum confinement effects is investigated in Sec. 6.5. Section 6.6 describes a method to determine band offsets between two amorphous semiconductors. Our findings are summarized in Sec. 6.7.

### 6.2 Technical details

The total energy and forces are calculated within DFT using the Generalized Gradient Approximation (GGA) with the PW91 functional.\textsuperscript{57} All calculations were performed with the Vienna \textit{Ab initio} Simulation Package (VASP).\textsuperscript{40,41} Electron-ion interactions are described using the projector augmented wave method.\textsuperscript{42,74} MD calculations were performed with a “soft” nitrogen potential and a 250 eV kinetic energy cut-off. For static calculations a 400 eV cut-off and “normal” potentials supplied with VASP were used. The performance of the potentials was tested on \(\alpha\) and \(\beta\) phases of \(\text{Si}_3\text{N}_4\). The calculated cell parameters were higher than experimental ones by less than 1%. The difference in cell parameters between the “soft” and “normal” potential was \(\sim 0.1\%\). During the whole MD run and the relaxation, we use only the \(\Gamma\) point for Brillouin zone sampling. When calculating the density of states of the relaxed structures the Brillouin zone is sampled with a \(2 \times 1 \times 2\) Monkhorst-Pack mesh.\textsuperscript{76} In both cases a Gaussian smearing with a width of 0.05 eV is used. Molecular dynamics calculations were performed with a 1 fs time step.
6.3 Preparation of the structure

A model of the multilayer was prepared by merging cells of a-Si:H and a-SiN:H. This results in the formation of two interfaces because of the periodic boundary conditions used throughout all calculations. Both constituent cells were prepared previously with the “cooling from liquid” approach and entirely from first-principles.\textsuperscript{115,177} This method is found to generate structures with the short range order in a good agreement with experiment. The composition and density of the cells are based on experimental values. The silicon cell Si\textsubscript{216}H\textsubscript{27} has a density of 2.0 g/cm\textsuperscript{3}. The nitride cell Si\textsubscript{194}N\textsubscript{194}H\textsubscript{85} has a density of 3.0 g/cm\textsuperscript{3}.\textsuperscript{125}

Originally the cells exhibited a positive pressure of 84\times10\textsuperscript{8} and 9\times10\textsuperscript{8} Pa for the silicon and nitride respectively. The dimensions of the cells were adjusted, in order to prevent the expansion of the nitride cell into the silicon, during the formation of the interface. First both cells were expanded isotropically from 16.593 to 16.972 Å (by 2.3\%). Next the silicon cell was compressed by 0.49 Å (2.9\%) in the \textit{y} direction. Conversely, the nitride cell was \textit{expanded} by the same amount. This was done to minimize the combined total energy of the two cells. Finally, we shift the cells relative to each other along the interface plane in order to prevent atoms to be too close in the newly formed interface. We will refer to this initial ML model as the “I” cell. In the next step we have performed a relaxation and we will denote this cell with the letter R. In order to form a more realistic ML model we perform an annealing cycle at 1818 K (see Fig. 6.1). This leads to a complete melting of the silicon but leaves the silicon nitride network unaltered, since it has a much higher melting temperature. At 1818 K we observe sufficient diffusion of atoms in the interface region. We let the system evolve for 4 ps. Next the cell is cooled back to room temperature. We utilize two different cooling rates: 1.380 K/fs and 0.023 K/fs, that lead to the “fast” and “slow” cells (F and S cells for short). After reaching 300 K we perform an additional 500 MD steps to calculate structural averages. Finally the cells are relaxed in order to calculate the electronic properties.

6.4 Structure on the atomic scale

The atomic-scale structure of the various ML models is dependent on the preparation procedure employed. The model I, being the simplest one, is formed by merging a cell of silicon and nitride without further treatment.
Model R is formed by relaxation of atoms in model I into the nearest local minima. We therefore expect the interface to be still atomically sharp. Unlike the previous models, during preparation of the F and S cells, the atoms had time to rearrange into a more energetically favorable structure.

The density profile in Fig. 6.2 gives us the first impression about the differences between the models. We observe that after the annealing (models F and S) the density in the middle part of the silicon cell increases. Another visible feature is a depression caused by a void in the nitride cell around 21 Å. The void was present already in the initial model, but gets further pronounced after the anneal cycles. We also notice that there is a dip in the density at the silicon side of both interfaces.

To investigate the differences between the models in more detail we plot concentration profiles of the R, F and S cells with respect to the I cell in Fig. 6.3. This will allow us to identify regions where atoms diffuse into. After the fast and slow anneal the concentration of silicon increases in the middle part of the silicon cell. Hydrogen atoms, by contrast, diffuse into the silicon side of the interfaces.

In Figure 6.4 we visualize locations, from where the mobile silicon and hydrogen atoms originate. For silicon, we select the mid part of the a-Si:H cell (where the curves of Fig. 6.3 are positive) and plot a concentration profile of atoms that diffused into this region. We observe that for both annealed cells silicon atoms diffuse from the edges of the cell into the middle part. A small portion of atoms leaves also the nitride cell. In the case of
Figure 6.2: Density profile in a direction perpendicular to the interface: I cell (black dashed line), R cell (red solid line), F cell (green solid line) and S cell (blue solid line). Each atom is overlayed with a Gaussian with a variance of 1 Å. The silicon cell is repeated in order to see both interfaces more clearly.

Figure 6.3: Concentration profiles of the R, F and S cells with respect to the I cell. Concentration of silicon (black line), nitrogen (green line) and hydrogen atoms (red line). Atoms are represented as Gaussians with a variance of 1 Å and area of 2 Å². The silicon cell is repeated in order to see both interfaces more clearly.
hydrogen, the selected regions are at the interface, closer to the a-Si:H side. There are, however, two interfaces that we have to distinguish. We find that hydrogen diffuses just the opposite way as silicon: from the mid part of the silicon cell towards the interface. Also a considerable part of hydrogen comes from the edges of the nitride cell.

In line with the experiments of Roxlo et al.\textsuperscript{157} and Matsumoto et al.\textsuperscript{158}, our molecular dynamics calculations point at an increased hydrogen concentration at the interface. Our structural models were, however, prepared in a way that has little to do with a plasma deposition and it is difficult to use them to explain the order-of-deposition differences. They rather demonstrate that at elevated temperatures, hydrogen becomes mobile and diffuses through the amorphous network. Subsequently a part of the hydrogen becomes trapped at the interface region where it passivates defects.

Different ML models contain a varying number of defects. By defect we mean an atom that departs from its normal coordination. Thus Si, N and H atoms that are other than 4-fold, 3-fold and 1-fold coordinated respectively are considered to be defects. Two atoms are bonded when closer than a certain cut-off distance. The cut-off distances are taken as the posi-
CHAPTER 6. THE SILICON/NITRIDE MULTILAYER

Table 6.1: A summary of defects present in different samples. Artificial Si–Si bonds inside “square structures” are discarded from the count. S2 denotes a 2-fold coordinated silicon atom. Column denoted by $D_{tot}$ contains the total number of structural defects. The last column contains cohesive energies of cells per atom in eV.

<table>
<thead>
<tr>
<th>cell</th>
<th>Si2</th>
<th>Si3</th>
<th>Si5</th>
<th>Si6</th>
<th>H0</th>
<th>H2</th>
<th>N1</th>
<th>N2</th>
<th>N4</th>
<th>$D_{tot}$</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso.</td>
<td>16</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>30</td>
<td>-6.188</td>
</tr>
<tr>
<td>I</td>
<td>3</td>
<td>40</td>
<td>21</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>4</td>
<td>14</td>
<td>1</td>
<td>91</td>
<td>-5.980</td>
</tr>
<tr>
<td>R</td>
<td>0</td>
<td>23</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>6</td>
<td>46</td>
<td>-6.139</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>13</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>8</td>
<td>39</td>
<td>-6.157</td>
</tr>
<tr>
<td>S</td>
<td>0</td>
<td>8</td>
<td>5</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>20</td>
<td>-6.205</td>
</tr>
</tbody>
</table>

The Si–Si and Si–N cut-offs are set to 2.65 Å and 2.00 Å respectively. We do not find any N–N and the corresponding first neighbor peak is missing. The Si–H and N–H cut-off distances are set to 1.65 Å and 1.15 Å. We find also several H$_2$ molecules and the H–H cut-off distances is set to 0.85 Å. Although this simple method of identifying defects based on measuring distances between atoms works reasonably well for a-Si:H, for the nitride it does not. The non-stoichiometric nitride contains certain “square structures” where two Si atoms are not bonded even when they are within their cut-off distance.* We account for this fact and discard these artificial bonds from the defect count in Table 6.1. As expected the initial cell I contains the most defects, among them defects with a high formation energy: isolated H and N atoms and 6-fold coordinated silicon atoms. The slow anneal is quite effective in removing defects. The S cell contains even a smaller number of defects that the isolated cells, resulting in a defect concentration of ~3 at. %. Additionally the cell S is lower in energy by 0.225 eV per atom compared to the I cell. The difference between the cohesive energies of the different interface models with respect to the combined cohesive energy of the isolated cells, gives an estimate of the interface energy. Cells I, R and F have all a positive interface energy while cell S has a negative interface energy of $-0.35$ J/m$^2$.

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*After subtracting atomic charge densities from the total density, we do not observe charge accumulation between Si atoms that form square structures.
6.5 Quantum confinement

The electronic structure of an amorphous semiconductor differs from its crystalline counterpart. Disorder leads to the formation of localized states (tail states) at the band edges. Tail states are separated from extended states by the mobility edge. The above mentioned features were observed previously in atomistic models of a-Si:H. A convenient way to visualize tail states is to plot the participation ratio of each Kohn-Sham orbital $\psi^{KS}$ as a function of its energy. The participation ratio is a measure of localization of $\psi^{KS}$ and is defined as follows:

$$p = \frac{M_1^2}{M_0 M_2},$$

where $M$ is defined as

$$M_k = \sum_{i=1}^{N} \rho_i^k.$$

$p_i$ denotes charge density on atom $i$. The density is evaluated within spheres centered on each of the $N$ atoms. The size of the spheres is set to the covalent radius: 1.11 and 0.37 Å for silicon and hydrogen respectively. For a strongly localized orbital $p = 1/N$, while a plane-wave has a participation ratio of one. Figure 6.5 contains a participation ratio plot of the silicon cell, used to construct the initial model of the interface. We approximate the extended and tail states with linear functions. The position of the mobility edge is determined as an intersection of the lines. For the mobility gap we obtain a value of 1.93 eV, quite close to the experimental value of 1.83 eV. We wish to stress, however, that although this similarity is fortunate it is merely a coincidence. This is because DFT, being a ground state theory, usually underestimates band gaps. Secondly, the experimental mobility gap is determined by transport or optical measurements and not by measuring the localization of the wave-function (at least not directly). In other words, it is not known at what value of the participation ratio the measured gap occurs. Although the above described method to determine the band gap of a-Si:H gives correct values for the wrong reason we will use it in the following discussion on confinement effects. In our opinion the band gap obtained in this way is better defined than the gap determined from DOS plots. Secondly it is likely that the concentration of tail states is overestimated in our atomistic model. Thus determining the band gap from a DOS plot will lead to underestimation of the gap.
Let us first investigate quantum confinement effects in a-Si:H surrounded by vacuum. We utilize the initial ML model and replace the nitride part with vacuum, thus creating a 16 Å silicon slab. Removing 4 Å of silicon on both sides will result in an even thinner slab (8 Å wide). Next the surfaces of both slabs are saturated with H atoms. Note that thanks to the way these cells were constructed, there exists a region (8 Å wide) in all three cells (bulk, 16 slab, 8 slab) that has an identical atomic structure. Figure 6.6 contains participation ratio curves of the 3 cells. The curves are aligned on the core potential of a silicon atom located approximately in the middle of the three silicon slabs. The surroundings of this atom are the same throughout all cells. We observe that the gap increases with a decreasing slab thickness. For the 16 and 8 Å slab the gap is 2.52 and 3.42 eV respectively. These values together with the bulk value can be fitted with the infinitely deep quantum well model. The fit results in a relative mass of 0.8. We also notice that the opening of the gap is symmetrical.

The results, on a-Si:H in vacuum, point to strong confinement effects that are to be expected for a deep quantum well. The situation is different in multilayers, where the depth of the well for electrons (holes) is determined by the conduction (valence) band offset at the interface. Figure 6.7 shows participation ratio of a-Si:H in the initial and slow ML model. We find that, although there is some variation between the models, the confinement in the ML is still strong. The initial and fast models give band gaps
Figure 6.6: a-Si:H surrounded by vacuum. Participation ratio curves of bulk silicon (black line), 16 Å slab (red line) and 8 Å slab (green line). Dots mark the position of the mobility band edges. Curves aligned at the core potential of a silicon atom.

Figure 6.7: a-Si:H surrounded by silicon nitride. Participation ratio of bulk silicon (black line), silicon in the initial ML model (red line) and silicon in the slow ML model (green line). Dots mark the position of the mobility band edges. The alignment along the energy axis is arbitrary.
of 2.67 and 2.58 eV respectively. For the relaxed and slow model we find smaller band gaps (2.31 and 2.33 eV respectively). These are comparable to the experimental value of 2.27 eV (for 13 Å well thickness) measured in a ML with an identical composition as our models.\textsuperscript{154}

### 6.6 Band offsets

#### 6.6.1 The average potential approach

First-principles methods have been successfully applied to calculate band offsets between two crystalline materials.\textsuperscript{24,179} Here a model of the interface is constructed by merging several conventional unit cells of material A followed by cells of material B. This supercell is then used to extract the offset of the electrostatic potential between the two materials. The atomic-scale oscillation of the electrostatic potential is conveniently filtered out by averaging in a slab with a geometry of the conventional unit cell. When sufficiently far away from the interface, the averaged potential attains its bulk value. The band offsets are finally obtained as rigid shifts of the electronic structure of material A and B by the potential offset. The position of the valence and conduction band edges are taken from separate calculations on the bulk materials.

The above described approach is, however, not suitable for amorphous solids. Because of the use of annealing cycles the interface models have different structures than the isolated cells. We have to investigate whether we can obtain the offsets as \textit{rigid} shifts of the electronic structure of the bulk materials. From Figure 6.8 we see that for the F and S cells this is indeed not possible. In this cases the valence band of a-Si:H is broader compared to the bulk material.\textsuperscript{1} The valence band in the F and S cells is higher by 0.36 and 0.24 eV respectively as compared to the isolated a-Si:H cell. For silicon nitride the widths of the bands seem to be unaffected by the annealing (see Fig. 6.9). This is to be expected, since during the annealing the temperature was controlled in such a way as to melt the silicon but to leave the nitride unaltered.

Another difficulty one encounters in amorphous solids is related to the averaging of the electrostatic potential. Here the averaging will not filter

\textsuperscript{1}Note, that the DOS curves of the F and S cells reach higher values. Comparing normalized DOS curves, however, still leads to a broadened valence band of the F and S cells.
Figure 6.8: Density of states of a-Si:H calculated in a 8 Å wide slab. Different curves refer to: isolated silicon cell, I, R, F and S cells. In all cases the slab is positioned in the center of the a-Si:H cell.

Figure 6.9: Density of states of a-SiN:H calculated in a 8 Å wide slab. Different curves refer to: isolated nitride cell, I, R, F and S cells. In all cases the slab is positioned in the center of the a-SiN:H cell.
out the oscillations in the potential completely. This is because our silicon and nitride cells are not composed of several conventional unit cells. Naturally using a larger averaging slab will damp the oscillations. In Figure 6.10 we calculate the standard deviation of the potential as a function of the slab thickness. For a slab 8 Å wide the deviation in the potential becomes 0.1 eV for both materials. The oscillations are relatively large and the value of 0.1 eV is an additional source of error in the calculation of the band offset.

### 6.6.2 The local DOS approach

A more straightforward approach for calculating band offsets makes use of the site-projected density of states. The DOS is projected on spherical harmonics within spheres that are centered on the atoms. Here we use spheres with diameters corresponding to the covalent radii of atoms: 1.11, 0.75 and 0.37 Å for silicon, nitrogen and hydrogen respectively. This method also circumvents the necessity to determine the averages of the electrostatic potential. In Figure 6.11 the site-projected DOS of cell S is averaged in 3 Å wide slabs parallel to the interface plane. We observe a symmetrical opening of the band gap when going from the bulk silicon to the bulk nitride regions. It also appears that the valence and conduction band edges converge to their bulk values approximately 3 Å from the interface border. Irregularities of the order of 0.3 eV form in the nitride cell.
Figure 6.11: Position resolved DOS of cell S along the y-axis. The DOS is in arbitrary units. The silicon cell is repeated in order to see both interfaces more clearly. Interfaces are marked by vertical lines.

They originate from the inhomogeneities that are intrinsic to the silicon nitride with this particular composition.

To get a more quantitative view of the valence band offset we plot the DOS in a 8 Å wide slab positioned in the center of the silicon and nitride cells making up the ML model (see Fig. 6.12). From the S cell we obtain a valence band offset of 0.68 eV. Note, that the value is quite independent on the DOS value, because the slopes of the valence edges are similar in both materials. It is important to realize that the calculated offset refers to confined and not bulk a-Si:H, the band gap of which is 0.40 eV smaller. Although the position of the valence bands is described correctly by DFT, the position of conduction bands is not. To calculate the conduction band offsets we will use the experimental band gaps of 1.83 and 2.85 eV for silicon and nitride respectively. Drawing the complete band diagram leads to a rather surprising conclusion (see Fig. 6.13). The confinement effects originate solely from holes, since the conduction band is higher in the silicon than in the nitride. Assuming that the opening of the gap due to confinement is symmetrical, will allow us to calculate band offsets between bulk materials. Employing the experimental band gaps again, results in a valence and conduction offset of 0.88 and 0.14 eV respectively.

\[\text{\textsuperscript{\dagger}This is only true when using an exact exchange-correlation functional.}\]
Figure 6.12: Density of states of bulk silicon (red line) and nitride (black line) in the slow ML model. The curves are calculated from site-projected DOS summed in slabs 8 Å wide. Calculated with Gaussian smearing of 0.05 eV.

Figure 6.13: Band diagram of the a-Si:H/a-SiN:H multilayer. All values are in electron volt.
6.7 Conclusions

Using DFT molecular dynamics we have prepared an atomistic model of the a-Si:H/a-SiN:H multilayer. The preparation procedure has a dramatic effect on the structure of the model. In particular, annealing reduces the number of defects and the cohesive energy. In our model containing 716 atoms, the cooling rate of 0.023 K/fs resulted in a ~3 at. % defect concentration and a negative interface energy of -0.35 J/m². Annealing at elevated temperatures promotes hydrogen to a mobile state. A part of the hydrogen becomes trapped in the interface region, where it passivates defects.

We have investigated quantum confinement of charge carriers in slabs of a-Si:H in vacuum and in the ML structure. Analysis of the participation ratio shows that there are considerable confinement effects in both cases. The increase of the band gap in the case of the ML is comparable to the experimental result on an identical system.

The first-principles models were used to calculate band offsets of an amorphous/amorphous interface for the first time. The standard method used to extract offsets for crystalline interfaces, could not be applied in this particular case. The reasons are two fold. The offsets cannot be calculated as rigid shifts of the bulk band structure due to annealing, that affects the structure. Secondly, the variation in the average potential is substantial and would introduce additional errors to the offsets. To circumvent the above mentioned difficulties, we calculate the offsets from the site-projected DOS. The valence band offset between the confined silicon and the nitride is 0.68 eV.

Using the experimental band gaps results in a negligible conduction band offset in the ML system. From this follows that the quantum confinement effects in the ML originate from holes only. The calculated band offsets between bulk silicon and bulk nitride are 0.88 and 0.14 eV for the valence and conduction bands respectively.
Chapter 7

Conclusions & Outlook

In this chapter we summarize the main results of this thesis. We also point out several topics where future research could be directed.

The main conclusion of Chapter 3 is that one can prepare good quality a-Si:H models by the cooling from the liquid method. Our models are an improvement over the models from the past, which often contained remnants of the liquid structure. This was manifested by over-coordination and a high number of structural and electronics defects. The reason for the improvement is quite simple: one has to use slower cooling rates. An a-Si:H model containing ~200 atoms requires a quench that lasts for ~100 ps. Fortunately, this time range can be reached with first-principles molecular dynamics and with the present computer power.

An important issue when working with structural models is their validation. At present this is mostly done by comparing pair-correlation functions (either in the direct or reciprocal space) with experiment. Even for a-Si:H, which is the most studied amorphous semiconductor, there are considerable differences between the measured curves. Diffraction experiments on a-Si:H prepared at different conditions and measured to higher wave-vectors would be beneficial for the progress in the field.

Atomistic models are in many ways complementary to the experiment. A good example are defects in a-Si:H that are discussed in Chapter 4. Experiments such as deep-level transient spectroscopy or Electron Paramagnetic Resonance (EPR) provide a global averaged view of the defects. One can extract the distribution of defect states in the band gap or measure the total concentration of defects. To make the link to the microscopic structure of the defect is, however, difficult. This is where models can be
helpful. One can calculate the position of the defect state in the band gap or the EPR signal for different defect models and different surroundings and thus interpret the measurement.

The dominant defect in a-Si:H is believed to be the 3-fold coordinated Si atom, the so called “dangling bond”. In Chapter 4 we have calculated formation energies of the dangling bond in the negative, neutral and positive charge state. We find that the majority of the defects can exist in all three charge states (depending on the Fermi level position), but some of them exist only as charged. A rather surprising result is that our models contain also different defects: 5-fold Si and 2-fold H. Both defects were found to induce states in the band gap. Do these defects exist in any appreciable quantities? This needs further investigation. The knowledge about the energetics of defects could also bring us closer to the microscopic understanding of the Staebler-Wronski effect.

Compounds of a-Si:H with carbon and nitrogen are less studied than the pure material. In Chapter 5 we investigate a silicon rich phase of a-SiN:H at two very different densities. We describe the short-range order and calculate the pair-distribution functions. The Si-Si bond states are located at the band gap edges. This explains why the band gap increases with increasing nitrogen content. The onset of phase separation in the dense nitride is observed.

In the last chapter we prepare a model of the silicon/silicon nitride multilayer with the very same composition as used in the SELECT absorber. We find that annealing the multilayer leads to trapping of hydrogen at the interface defects. Perpendicular transport of charge carriers through the structure is closely related to the band offsets between the two materials. We find that holes experience a barrier of $\sim 0.7 \text{ eV}$ while electrons can move relatively freely through the structure. In literature one can find conflicting reports on the existence or magnitude of quantum confinement effects in amorphous multilayers. Our model allows us to study confinement effect directly, without the need to optical or transport measurements. We find that the confinement effect is indeed present and has a magnitude close to the experimental energies.
Bibliography


Summary

Crystalline silicon is probably the best studied material, widely used by the semiconductor industry. The subject of this thesis is an intriguing form of this element namely amorphous silicon. It can contain a varying amount of hydrogen and is denoted as a-Si:H. It completely lacks the neat long range order of the crystal, yet its structure is not random. Almost all silicon atoms have four neighbors and the average bond angle is identical to the tetrahedral angle in the crystal. Order is thus preserved over several bond lengths.

The motivations to study a-Si:H are two-fold. Firstly some of its properties are different from the crystalline form and we do not understand them completely. For example, the electronic properties degrade after exposure to intense light, but can be recovered reversibly by heat treatment. The microscopic process of this is not known.

Secondly, research on a-Si:H is motivated by its applications. These are mostly large area devices such as liquid crystal displays and solar cells. The latter are in use already today, the former are waiting to be widely used in future. Amorphous semiconductors can be deposited over large areas from vapor. On the other hand, the size of c-Si devices is limited by the much smaller size of the wafers. The production of a-Si:H is also cheaper and consumes less energy. Unlike its crystalline counterpart a-Si:H has a direct band gap, leading to an increased light absorption. Consequently, a-Si:H solar cells are \( \sim 1000 \) times thinner than c-Si cells, resembling more a foil than a semiconductor device.

The methods used in the thesis are computational, largely relying on algorithms and powerful computers. The structural models are atomistic, where the interaction between electrons and nuclei is treated on the level of Density Functional Theory. This is a first-principles methods, meaning that it does not use any adjustable parameters. The chemical bonding, even of complex structures is described accurately. Calculation of total
energies and forces allows us to find equilibrium structures and perform molecular dynamics calculations.

The models of a-Si:H are prepared by cooling a melt to room temperature. This method resembles the preparation of glasses. We find that the structure is strongly influenced by the cooling rate. Using slower cooling rates we improved existing models that contained excessive strain and a high defect concentration. Using a cooling rate of $\sim 0.02 \text{ K/fs}$ we were even able to prepare small defect-free models. The structure was in good agreement with available neutron scattering data. Calculated density of states shows a pronounced band gap.

After the generation of structural models we turn our attention to defects. Defects in an amorphous solid are defined as atoms that deviate from the normal coordination. We find 3-fold and 5-fold coordinated Si atoms and 2-fold coordinated H atoms. We focus only on the 3-fold coordinated Si, also called the dangling bond (DB), that is believed to be the major defect in a-Si:H. We have calculated formation of the DB defect in the negative, neutral and positive charge state. By averaging over 25 distinct DB models we find a considerable spread in the energies of 0.2 eV. Another related property of a defect is its correlation energy $U$. A positive value of $U$ means that we have to invest energy to add an extra electron to the defect. The size and sign of $U$ are still a subject of controversy. On average we find a positive $U$ value of 0.1 eV. Four models, however, have a negative correlation energy, suggesting large relaxations in the defect structure.

Amorphous silicon readily forms compounds with nitrogen and carbon. We have investigated silicon-rich nitride (a-SiN:H) at two different densities of 2.0 and 3.0 g/cm$^3$. Features in the pair-distribution functions can be related to “square structures”. These are planar structures consisting of two Si in opposite corners of a square and two N in the remaining corners. The dense phase shows signs of phase separation into silicon and stoichiometric nitride. Both valence and conduction band edges are dominated by Si states. This is corroborated by the fact that by increasing the nitrogen content the band gap of the nitride can be varied from 1.8 to 5.3 eV.

Recently there has been a considerable interest in man-made materials. Examples are multilayers (ML) formed by two semiconductors with a different band gap. By adjusting the thickness of the small band gap material (the well) one can tune the band gap of the ML due to quantum confinement effects. This concept is well established in crystalline semiconductors. The existence of quantum confinement in amorphous struc-
tasures is, however, being still debated. Using models prepared previously we have constructed a model of a silicon/nitride ML. This allowed us to study confinement effects directly without using transport or optical measurements that can obscure the observations. Comparing our model to an experimental system with the same composition gave almost identical band gaps. This confirmed the existence of quantum confinement in a amorphous multilayer. The calculation of band offsets between the materials revealed that there is almost no barrier for the electrons and the confinement originated solely from holes.
Samenvatting

Kristallijn silicium behoort waarschijnlijk tot één van de best bestudeerde materialen en wordt op brede schaal toegepast in de halfgeleider industrie. Het onderwerp van dit proefschrift is een intrigerende vorm van dit element, die bekend staat als amorf silicium. Dit materiaal kan een variabele hoeveelheid waterstof bevatten en wordt ook wel a-Si:H genoemd. Hoewel de bij een kristal aanwezige ordening in amorf silicium over lange afstanden ontbreekt, is de structuur niet willekeurig. Vrijwel alle silicium atomen hebben vier buuratomen en de gemiddelde hoek tussen de binding is identiek aan de tetraëdische hoek in het kristal. De ordening blijft dus behouden over een afstand van enige bindingslengtes.

Er zijn twee redenen waarom a-Si:H bestudeerd wordt. Allereerst worden een aantal verschillen in eigenschappen, ten opzichte van de kristallijn vorm, nog niet volledig begrepen. De elektronische eigenschappen van het materiaal verslechteren na blootstelling aan licht met hoge intensiteit, dit effect is kan men ongedaan maken met een warmtebehandeling. De microscopische processen van dit fenomeen zijn onbekend.

Een tweede motivatie voor onderzoek naar a-Si:H zijn de toepassingsmogelijkheden. Dit zijn voornamelijk apparaten met een groot oppervlak, zoals Liquid Crystal Displays (LCD’s) en zonnecellen. De laatstgenoemde worden reeds toegest, terwijl de LCD’s hun opwachting maken om in de toekomst op grote schaal te worden gebruikt. Amorfe halfgeleiders kunnen op grote oppervlakten worden aangebracht vanuit de dampfase. Componenten van c-Si zijn daarentegen beperkt door de veel kleinere afmetingen van wafers. Daarbij is de productie van a-Si:H goedkoop en gebruikt minder energie. Anders dan zijn kristallijne tegenhanger, heeft a-Si:H een directe bandafstand, wat resulteert in een verhoogde lichtabsorptie. Hierdoor zijn a-Si:H zonnecellen ~ 1000 keer dunner dan c-Si cellen, waardoor deze meer op folie lijken dan op een gebruikelijk component van halfgeleiders.
De methoden die worden toegepast in dit proefschrift zijn theoretisch en maken gebruik van complexe programmatuur en supercomputers. De structuur-modellen zijn op atomistisch, waarbij de interactie tussen de elektronen onderling en de kernen behandeld wordt met de dichtheidsfunctionaaltheorie. Deze theorie maakt geen gebruik van parameters die aangepast worden. Chemische bindingen worden accuraat beschreven, zelfs op het geval van complexe structuren. Met de berekening van de totale energie en de krachten op atomen, kunnen evenwichts-structuren gevonden worden en moleculaire dynamica berekeningen uitgevoerd worden.

De modellen van a-Si:H worden gemaakt door een smelt tot kamertemperatuur af te koelen. Deze methode komt overeen met de vervaardiging van glas. Het blijkt dat de structuur sterk wordt beïnvloed door de snelheid waarmee men afkoelt. Door gebruik te maken van lagere afkoelsnelheden, is het gelukt om bestaande modellen, die een excessieve rek en een hoge concentratie van defecten hadden, te verbeteren. Door gebruik te maken van afkoelsnelheden van ~ 0.02 K/fs was het zelfs mogelijk om kleine, defect vrije modellen te maken. De structuur kwam goed overeen met experimenteel bepaalde data gemeten met neutronenverstrooiing. De berekende toestandsdichtheden tonen een goed gedefinieerde bandafstand.

Na de vervaardiging van de structuurmodellen wordt de aandacht gericht op defecten. In amorfe vaste stoffen worden defecten gedefinieerd als atomen die afwijken van de normale coördinatie. Er worden Si atomen aangetroffen met een drievoudige en vijfvoudige coördinatie en H atomen met een tweevoudige coördinatie. Aandacht werd vooral besteed aan drievoudig gecoördineerde Si atomen, ook bekend als vrije valentiebindingen (VB). Men veronderstelt dat dit het voornaamste defect is in a-Si:H. De formatie energie van het VB defect is berekend voor de elektrisch negatieve, neutrale en positieve toestand. Door te middelen over 25 verschillende VB modellen, wordt een aanmerkelijke spreiding gevonden van 0.2 eV in de energie. Een gerelateerde eigenschap is de correlatie energie U van de defecten. Een positieve waarde van U betekent dat energie moet worden geïnvesteerd om een extra elektron toe te voegen aan het defect. De grootte en het teken van U zijn heden ten dage nog een controversieel onderwerp. Gemiddeld wordt er een positieve waarde gevonden voor U van 0.1 eV. Daarentegen hebben vier modellen een negatieve correlatie-energie, wat een grote relaxatie in de structuur van het defect suggereert.

Amorf silicium vormt gemakkelijk verbindingen met stikstof en koolstof. Silicium rijk nitriden (a-SiN:H) zijn onderzocht met twee verschillende
dichtheden (2.0 en 3.0 g/cm³). Specifieke kenmerken van de paar distributie functie kunnen worden gerelateerd aan “vierkante structuren”. Dit zijn planaire structuren die bestaan uit twee Si in tegenoverliggende hoeken van een vierkant en twee N in de overgebleven hoeken. De dichte fase laat tekenen zien van fase-scheiding in silicium en het stoichiometrische nitride. De bandkant van zowel de valentieband als de geleidingsband wordt gedomineerd door Si toestanden. Dit wordt bevestigd door het feit dat een toename van de hoeveelheid stikstof, leidt tot een bandafstand van het nitride variërend tussen de 1.8 en 5.3 eV.

Recentelijk is er een aanzienlijke interesse ontstaan voor door de mens ontworpen materialen. Voorbeelden hiervan zijn multilagen (ML) die gevormd worden door twee halfgeleiders met een verschillende bandafstand. Door de dikte te variëren van het materiaal met de kleine bandafstand (de put), kan de bandafstand van de ML afgestemd worden door het effect van kwantumopsluiting. Voor kristalline halfgeleiders is het algemeen geaccepteerd dat dit concept opgaat. Het bestaan van kwantumopsluiting in amorfe structuren wordt momenteel echter nog bediscussieerd. Met behulp van de eerder ontwikkelde modellen, is een model gevormd van silicium/nitride ML. Hierdoor werd het mogelijk om de effecten van opsluiting direct te bestuderen, zonder dat er gebruik te maken van transport- of optische-metingen. Een vergelijking van het model met een experimenteel systeem, met dezelfde samenstelling, resulteerde in vrijwel identieke bandafstanden. Dit bevestigt het bestaan van kwantumopsluiting in een amorfe multilaag. De berekening van het verschil in energie van de banden toont aan dat er bijna geen barrière bestaat voor de elektronen en alleen gaten de opsluiting merken.
Publications


Acknowledgments

Finally my thesis is finished and at this point I would like to thank all the people that supported me throughout my PhD.

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About the author

Karol Jarolimek was born on the 2nd July 1982 in Bratislava, Slovakia. From 1996 until 2000 he attended the Gymnasium of Ivan Horváth in his hometown. This was a secondary school providing a general education with an emphasis on the English language. In 2001 he enrolled in the Faculty of Electrical Engineering and Information Technology at the Slovak University of Technology. Later in his studies he decided to specialize in Physical engineering. He followed courses on solid-state and semiconductor physics, quantum mechanics, nuclear physics and particle accelerators. In 2007 Karol was awarded the title Ing. (engineer’s degree). His thesis dealt with point defect in crystalline silicon. As a part-time job, during his studies, he has developed the Fytopack program. The program is used by geo-botanist to check, convert and statistically evaluate their raw data. Shortly after receiving his title he moved to the Netherlands to work at Delft University of Technology as a PhD. researcher. The position was available within the SELECT project, that was initiated by the Photovoltaic Materials and Devices (PVMD) group at TU Delft, led by Prof. Miro Zeman. Karol, however, spent the first three years of his PhD. in the Electronic Structure of Materials group at the Radboud University Nijmegen, led by Prof. Robert de Groot. In this group Karol was working on theoretical models of amorphous semiconductors. In 2010 he moved to Delft to finish the work on the SELECT project and write a thesis. At present, Karol continues to work in the PVMD group, but this time as an experimental researcher. His goal is to fabricate a solar cell that contains a layer of silicon quantum dots to absorb light.