Structural Characterization
of
Amorphous Silicon

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Doctor of Philosophy
of
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Chapter 7

Atomic Scale Order
7.1 Introduction

To understand the structure of an amorphous material, the atomic scale order, or short-range order (SRO) characteristics, need to be thoroughly investigated. Investigation of the order on this scale up to \( \sim 8 \text{ Å} \) brings a wealth of information about parameters such as the bond-angle distortion, the mean bond-length, the mean bond-angle, the coordination number and further structural information.

For thick films of amorphous materials such as amorphous silicon neutron diffraction [12, 221] and/or X-ray diffraction [14] are usually employed in order to obtain the radial distribution function (RDF). However, these techniques cannot be used on small site-specific volumes such as the PI a-Si created by indentation. Therefore, the determination of the RDF by electron diffraction is highly advantageous [24]. In fact, one of the very first studies on the structure of a-Si concerning atomic arrangement was performed using electron diffraction [25].

Therefore, the real-space atomic scale structures of the pure forms of a-Si, ion-implanted and PI, were investigated using quantitative electron diffraction. Furthermore, the structural relaxation induced by thermal annealing on both these forms was investigated. As-prepared and relaxed ion-implanted a-Si have previously been characterized using high-energy X-rays [14], but not by electron diffraction. In addition, no detailed diffraction results, and therefore no real-space nearest-neighbour characteristics, have been reported for PI a-Si. The RDFs determined were investigated thoroughly for differences between the as-prepared and relaxed cases as well as between the as-indented PI and as-implanted a-Si, yielding some dissimilarities between the amorphous networks.

In addition, spectroscopy techniques such as Raman microspectroscopy can be used to access the vibrational properties of an amorphous film. These vibrational properties can be correlated very reliably to the structural order characteristics (see for example Refs. [13, 27–30] and references therein). As detailed in Section 2.2.1 in Chapter 2, \( \Gamma_{TO}/2 \) is empirically correlated to the bond-angle distortion \( \Delta \theta \), whereas the intensity ratio \( I_{TA}/I_{TO} \) is indicative of the order on a length-scale of 4-6 Å, the so-called intermediate-range order (IRO).

Raman microspectroscopy was performed on the a-Si films formed by magnetron-sputtering, ion-implantation and indentation in their as-prepared and relaxation annealed forms. The PECVD and laser-quenched a-Si were not investigated since their crystalline volume fraction does not allow extraction of their SRO characteristics by Raman microspectroscopy. The vibrational properties will be correlated to the bond-angle distortion and the order characteristics on the 4-6 Å length-scale. Sputtered and ion-implanted forms of a-Si have been well investigated by Raman microspectroscopy (see for example Refs. [27, 31, 135] for the former and Refs. [13, 16, 28] for the latter case). Little comparison however, has been performed between films formed by different means, but
Section 7.2: Experimental Details

measured under the same experimental conditions. Furthermore, the structural properties of sputtered films are well known to depend critically on parameters such as the substrate temperature or argon pressure [27], but the influence of ex situ thermal annealing after deposition has not been investigated in depth. Moreover, PI a-Si has not previously been investigated for its vibrational properties. Therefore, the structural characteristics gained from the vibrational properties before and after annealing will be presented and discussed in detail.

The results from the quantitative electron diffraction and Raman microspectroscopy are presented together in this chapter for two reasons. Firstly, both methods can probe the same SRO length-scales and secondly, the characteristics obtained by the two techniques are complementary to each other yielding in combination a more complete picture of the amorphous structure.

7.2 Experimental Details

Several different forms of a-Si were probed for their nearest-neighbour characteristics. In all cases the as-prepared forms as well as the films after a relaxation anneal were studied. All uniform films were investigated for the vibrational properties by Raman microspectroscopy, whereas only the pure films prepared by ion-implantation and indentation were characterized by electron diffraction. All of the studied films are summarized in Table 7.1. Note that for the atomic scale characteristics two different ion-implanted films, one ‘thick’ and one ‘thin’ are used. The different implantation conditions of these cases have been summarized in Table 3.3 in Chapter 3. However, the thickness of the ion-implanted layer is not expected to influence the experimental results. This is because back thinning of the plan-view samples to electron transparency results in investigation of only the top surface formed by the lowest implantation energy (i.e. the top ∼10 nm). Therefore, as long as a

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>Raman Microspectroscopy</th>
<th>Diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT sputtered</td>
<td>short-range order</td>
<td>-</td>
</tr>
<tr>
<td>300°C sputtered</td>
<td>short-range order</td>
<td>-</td>
</tr>
<tr>
<td>‘thick’ ion-implanted</td>
<td>short-range order</td>
<td>-</td>
</tr>
<tr>
<td>‘thin’ ion-implanted</td>
<td>-</td>
<td>RDFs</td>
</tr>
<tr>
<td>pressure-induced</td>
<td>short-range order</td>
<td>RDFs</td>
</tr>
</tbody>
</table>

Table 7.1: Different forms of a-Si characterized by Raman microspectroscopy and electron diffraction. Note that all these forms were investigated in their as-prepared and relaxation annealed form.
Chapter 7: Atomic Scale Order

surface is amorphized by a low energy implant (refer to Section 3.4 as to the importance of a surface implant), the characteristics of the amorphous network should be the same.

7.3 Electron Diffraction

The nearest-neighbour characteristics of the pure forms of a-Si, PI and ion-implanted, in their as-prepared and relaxed forms, were investigated using quantitative electron diffraction. Representative examples of the dampened reduced intensity function, \( \phi(k) \), obtained from the selected area diffraction patterns (SADPs) are shown in Fig. 7.1. The curves are offset by 0.2 for clarity. As detailed in Section 2.3.2, from these reduced intensity functions the reduced RDFs, \( G(r) \), can be calculated using equation 2.17. From these the RDFs, \( J(r) \), are in turn calculated using equation 2.13 with the mass densities measured by EELS (see Section 4.3.4 for details).

In this section the peak characteristics of the reduced RDFs will be discussed first, before the coordination number is determined from the RDF. Thereafter, the reduced RDFs will be analysed in more detail by peak fitting. Note that for all cases of peak fitting the values presented are the averages from the approximately five areas measured per form of a-Si and the uncertainty presented is the standard error. All these averaged values are tabulated in Appendix B, Section B.2.1 in the case of the coordination numbers and in Appendix B, Section B.2.3 for the in-depth analysis of \( G(r) \). In this section only the key results will be presented and discussed.

Figure 7.1: Reduced intensity function \( \phi(k) \) for as-implanted, relaxed implanted, as-indented PI and relaxed PI a-Si. Note that the functions are offset by 0.2 each for clarity.
7.3.1 Characteristics of the Reduced Radial Distribution Functions

Representative examples of reduced RDFs for the four different forms of a-Si are shown in Fig. 7.2(a). The reduced RDFs are offset by 1 for clarity. A reduced RDF of c-Si was calculated from a model with the same damping factor of 0.16 and is shown for comparison. Only the region of 0-6 Å was investigated in detail by peak fitting and thus a close-up of this region of the reduced RDF is shown in Fig. 7.2(b). The reduced RDF can be split into three regions for further investigation, whereby region A consists of the peak at 2.35 Å, region B of the peak at ∼3.8 Å and region C of the peak at ∼5.8 Å. These regions are also marked in Fig. 7.2(b). Note that the low-r region below the first peak is very noisy due to low-frequency oscillations in the reduced intensity functions, a common problem in electron diffraction. Therefore this region does not follow the line $G(r) = -4\pi r \rho_0$ as would have been expected theoretically.

The interpretation of the peak in region A is straightforward for c-Si as well as a-Si.

![Figure 7.2](image_url)

Figure 7.2: (a) The whole reduced radial distribution function $G(r)$ for c-Si, as-implanted, relaxed implanted, as-indented PI and relaxed PI a-Si; and (b) a close up with the regions of interest marked. Note that in part (a) the reduced RDFs are offset by 1 for clarity.
This peak is the first-nearest neighbour peak and thus corresponds to the four one-bond atoms and therefore to the coordination number and the mean bond-length. The situation however, is less clear for the other two regions. Region B clearly consists of two peaks in the crystalline case. Previous electron diffraction studies have regarded this peak in region B as consisting of one peak for the amorphous case [24]. But it should also be decomposed into two peaks in this current work since the peak visible in the reduced RDF is clearly asymmetric and cannot be fitted well with one Gaussian. This asymmetry and possible presence of a second peak within this region B has been noted in a previous X-ray diffraction study [14]. Therefore, this peak is presumably also composed of the second-nearest neighbour (the two-bond atoms) and the third-nearest neighbour (one of the two different types of three-bond atoms). Similarly, region C can be decomposed into two peaks, the fourth-nearest neighbour (the first four-bond atoms) and the fifth-nearest neighbour (the second type of three-bond atoms). Therefore, for the remainder of this thesis, the peak in region A will be referred to as peak 1, the peaks in region B as peaks 2 and 3 and the peaks in region C as peaks 4 and 5. For further details and justifications of the peak assignment refer to Appendix B, Section B.2.2.

In addition to the peaks in these major regions, a small peak between region A and region B at \( \sim 2.85 \text{ Å} \) can be observed. Although a similar peak has been observed in some studies on the structure of a-Ge (see for example Refs. [140, 222] and references therein), this peak is not usually observed for a-Si. This difference might be due to the fact that these previous studies were performed on thick films of pure a-Si [14] or on thin a-Si foils containing a significant amount of hydrogen [12, 25, 140]. Only one neutron-diffraction study on evaporated a-Si observed a similar peak although no comment on it was made [221] and the \( \sim 2 \) at.% of hydrogen present in this previous study make direct comparison difficult. Thus the origin of this peak remains unclear. The peak seems not to be caused by contamination or impurities however, and thus it might be tentatively assigned to surface effects due to the high surface-volume ratio of these very thin foils used in this present study. For further details on this small peak refer to Appendix B, Section B.2.2.

### 7.3.2 The Coordination Number

To obtain the coordination number (CN), the first peak of the RDF is investigated in detail. The RDFs, \( J(r) \), were calculated from the reduced RDFs, \( G(r) \), according to equation 2.17. The mass densities used are summarized in Table 7.2. These mass densities are converted to \([\text{atoms/Å}^3]\) from the mass densities measured by EELS\(^a\). The mass densities from EELS are consistent with a previous X-ray diffraction study performed on as-implanted and relaxed implanted a-Si by Laaziri et al. [14] who obtained mass densities of 0.049 atoms/Å\(^3\) for both cases. Examples of the derived RDFs are shown for each

\(^a\)See Section 4.3.4 for details on the mass density obtained by EELS.
Section 7.3: Electron Diffraction

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>Mass Density [atoms/Å³]</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-implanted</td>
<td>0.049</td>
<td>3.79 ± 0.11</td>
</tr>
<tr>
<td>relaxed implanted</td>
<td>0.049</td>
<td>3.83 ± 0.08</td>
</tr>
<tr>
<td>as-indent PI</td>
<td>0.050</td>
<td>3.65 ± 0.18</td>
</tr>
<tr>
<td>relaxed PI</td>
<td>0.048</td>
<td>3.69 ± 0.11</td>
</tr>
</tbody>
</table>

Table 7.2: Mass densities used for the calculation of $J(r)$ and average coordination number of as-prepared and relaxed ion-implanted and pressure-induced a-Si from Gaussian fits to the first peak of the resulting $J(r)$.

![Figure 7.3: Radial distribution function $J(r)$ for as-implanted, relaxed implanted, as-indent PI and relaxed PI a-Si.](image)

The CN is equivalent to the area under the first peak of the RDF as this area represents all atoms at a first-nearest neighbour distance from the atom at the origin. Thus, in order to determine the CN, the first peak of the RDF was fitted with a Gaussian using the package Origin [137]. This peak fitting was performed rather than integration of the area under the peak, as is more traditionally performed in electron diffraction, as asymmetries in the peak-shape may lead to the use of non-consistent boundaries for the integration and thus to inaccurate CNs. Moreover, the peak fitting is consistent with previous X-ray [14] and neutron diffraction studies [12] performed on amorphous silicon. During the fitting procedure the baseline of the fit was kept constant at 0 in order to ensure the whole area under the peak is included in the area of the fitted Gaussian. The thus obtained average CNs are also summarized in Table 7.2. In addition, the validity of this peak fitting
Figure 7.4: (a) Average coordination numbers of as-prepared and relaxed implanted and PI a-Si determined by Gaussian fits to the first peak of $J(r)$ and by integration. (b) Average peak width of the same peak from the fits and the integration. Note that the averaged values shown in both plots are tabulated in Appendix B, Section B.2.1.

approach was tested by also determining the CNs through integration. Both methods for CN determination yield the same values within error as shown in Fig. 7.4(a), thus validating the performed determination of the CNs.

Clearly, the CN of all forms of a-Si is lower than 4 indicating the under-coordination of the amorphous network. Ion-implanted a-Si is well known to be under-coordinated and CNs of 3.79 and 3.88 have previously been reported for the as-implanted and relaxed implanted case, respectively [14]. Thus the findings presented here are in excellent agreement with this previous study. It is noteworthy that these similar numerical results suggest that possible systematic errors such as the termination of $\phi(k)$ at relatively low $k$, the use of a damping function [14] and also the noise in the regime below the first peak do not appear to influence the determined CN significantly. In addition, both PI cases are also under-coordinated suggesting that this under-coordination may be inherent to the a-Si network rather than a specific feature of ion-implanted a-Si.

The width of the first peak of $J(r)$ was investigated using both methods, the Gaussian fitting and the integration. For both methods, the as-implanted and the relaxed cases exhibit the same peak width within error, whereas the peak width of the as-indented case is significantly increased as shown in Fig. 7.4(b). This increased peak width suggests a larger deviation in bond-length for the as-indented network.

Two main systematic errors could contribute to a false determination of the CNs, namely a wrong mass density $\rho_0$ or an incorrect determination of the number of scattering atoms $N$. The influence of these systematic errors is analysed in more depth in Appendix B, Section B.2.1. Both influences were found to be smaller than the statistical variation from the different areas. For example, an underestimation of the mass density by $\sim 4\%$ will only lead to an underestimation of the CN by $\sim 2\%$. The peak width was
not influenced at all by such a different mass density. The possible inaccuracy in the
determination of $N$ can originate from incorrectly performed normalization of $I(k)$ due
to, for example, multiple scattering events or low frequency oscillations. Although the
former case seems to be less significant as the films were kept very thin in order to avoid
such multiple scattering. Nonetheless, the influence of the number of scattering atoms
was investigated. The family of acceptable normalizations of $I(k)$ yield deviations from
the CNs as well as peak widths significantly lower than the standard error resulting from
the investigation of multiple areas per form of a-Si. Only the family of unacceptable nor-
malizations yield deviations of the same order as the standard error of the measurement.
Therefore it can be safely concluded that the statistical error of the approximately
five areas measured per form of a-Si is significantly larger than the systematic errors
possibly introduced by inaccurate $\rho_0$ and $N$. Thus, the observed under-coordination of all
amorphous networks when compared to c-Si is indeed relevant.

### 7.3.3 Detailed Analysis of the Reduced Radial Distribution Func-
tions

For further analysis of the peaks beyond the first-nearest neighbour, $G(r)$ rather than $J(r)$
was fitted. This was done for two reasons: firstly, in contrast to results from X-ray [14] or
neutron diffraction [12] the mass density cannot be determined from the same experiment
by fitting of the low $r$ regime of the $G(r)$ since, in this regime in the present work, $G(r)$
clearly does not follow the theoretically expected line $G(r) = -4\pi r\rho_0$. And it is this line,
or region, which was used to determine $\rho_0$ in the X-ray diffraction study. Therefore, the
mass density had to be obtained independently adding further uncertainties to the analysis.
Secondly, it is impossible to investigate the peaks beyond the first-nearest neighbour in
the RDF by careful peak fitting since the influence of the increasing density contribution
makes these fits successively more questionable. This is not a problem when fitting the
$G(r)$ as only the portion of the peaks above 0 may be fitted allowing easy distinction
between the different regions.

Thus, region A was fitted with one Gaussian and region B and region C with two
Gaussians each using the package Origin [137]. The only constraint on the fits was that
the baseline was not allowed to go below the minimum of the respective reduced RDF.
From these fits the peak positions, peak areas and peak widths were obtained. Note that
the averaged values are tabulated in Appendix B, Section B.2.2, whereas in this section
only the key results will be discussed.

The positions for the different peaks are the same within error for all forms of a-Si with
the possible exception of the second peak. In this case the relaxed forms may display a
slightly higher position than the as-prepared forms. The position of the first peak is also
the same as for c-Si in all amorphous cases indicating the same mean bond-length for
a-Si and c-Si. The positions of the two- and three-bond atoms (i.e. the second-, third- and fifth-nearest neighbours) are lower for all a-Si cases than observed for c-Si whereas the position of the first four-bond atoms (the fourth-nearest neighbours) is higher in all a-Si case. This may suggest that structural order dissipates with the fourth bond in all cases.

From the positions of the first and second peaks the mean bond-angle \( \bar{\theta} \) was calculated for each area using Eq. 2.18. This yielded on average 103.1 ± 1.1° and 103.0 ± 1.7° for as-implanted and as-indented PI a-Si, respectively, and 104.5 ± 0.8° and 105.2 ± 0.9° for relaxed implanted and PI a-Si, respectively. The deviation from the perfect tetrahedral angle of 109.45° might be slightly larger in the as-prepared cases, possibly suggesting less ordered networks for these forms. However, the uncertainty is too large to conclude this with any confidence. This large uncertainty also partially prevents the calculation of the bond-angle distortion \( \Delta \theta \) from the data using Eq. 2.19. The further reason for the inability to determine \( \Delta \theta \) in this present study is the lack of experimental data from a polycrystalline sample taken under identical experimental conditions as the peak width from such an RDF would be needed in order to correct for thermal smearing due to phonons [12].

Interestingly, significant differences between the different forms of a-Si are observed when the peak areas are considered. These peak areas are consistently smaller in the as-indented case, but the same within error for the as-implanted and both relaxed cases. In contrast, the peak width appears to be the same for all networks. This suggests a difference between the as-indented and other cases as the same peak width, but smaller peak area indicates a different peak shape. Therefore, from these peak areas and peak widths the peak heights were calculated. As expected the peak heights are also consistently smaller for the as-indented case than for the other three cases. Note that these differences are not visible by eye (i.e. in Figs. 7.2 and 7.3), but are consistently detected by peak fitting for all areas investigated. In order to capture this combination of similar peak width
but different peak height, the ratio of peak height to peak width was calculated and the averaged ratios are shown in Fig. 7.5(a). Note that these ratios are plotted on a log scale as the ratios encompass three orders of magnitude. The as-implanted and both relaxed cases are essentially the same within error. The ratio for the as-indented case, however, is consistently lower. This clearly indicates further differences in the as-indented network when compared to the other networks. Also note that the ~2% higher mass density of as-indented PI a-Si is not expected to play a significant role since the difference in this ratio is in the order of 50%.

In addition to this peak height/peak width ratio, the ratios of the different peak areas to each other were investigated for each form of a-Si. It is of interest to investigate the ratio of one area to another as they are independent of the differences in mass densities. Most of these ratios (such as peak 2/peak 3 or peak 2+3/peak 4+5) were the same within error for all forms of a-Si. However, in the case of the ratio of peak area 4 to peak area 1 and the ratio of peak area 4 to the area under region B (i.e. the sum of peak area 2 and 3), the as-indented case also proved different to the other forms of a-Si studied as shown in Fig. 7.5(b). While the as-implanted and relaxed cases are the same within error, the ratio is clearly lower for the as-indented case.

### 7.3.4 Interpretation

In summary, quantitative electron diffraction has revealed new insights into the differences between the as-indented PI a-Si and the other amorphous networks.

Determination of the coordination number has shown the under-coordination of all networks. The same analysis revealed an increased width of the first peak of the RDF for as-indented PI a-Si while the three other networks were the same. A detailed analysis of the reduced RDF has revealed that although the mean bond-length of all forms of a-Si is the same as that of c-Si, the mean bond-angle is clearly different. Additionally, analysis of the ratio of the peak heights to peak widths suggests a difference for the as-indented network as the ratio was lower by a factor of two. This difference is also observed in the ratio of the area under peak 4 to other areas as also here as-indented PI a-Si displays a significantly lower ratio.

Note that although differences between the as-implanted and relaxed cases have previously been observed by X-ray diffraction [14] no differences were observed in the current study. This behaviour is probably due to the higher ‘noise’ in the data presented here and also the lower range of \( k \) investigated. Filtering of \( \phi(k) \) for low-frequency oscillations might remove some of these experimental artifacts and would highlight differences between the as-implanted and relaxed networks. This was not done in the present study, but is planned for subsequent research. Interestingly, despite these issues it is clear that some structural ordering occurs upon annealing of PI a-Si as indicated by the fact that the
relaxed PI a-Si becomes indistinguishable from both implanted cases.

The findings from this quantitative electron diffraction study are consistent with a less ordered network for the as-indented PI a-Si. For example, the increased width of the first peak in the RDF indicates a larger spread in bond-length even if the mean bond-length is similar. In addition, the reduced peak areas with the same peak width, in the reduced RDFs may also suggest a larger spread in nearest-neighbour distances than in the other three cases. Since the number of atoms in the as-indented networks is higher than in the other three cases (as indicated by its increased mass density), this may suggest that more atoms are sitting on ‘in-between’ sites rather than being tetrahedrally bonded. Such a less ordered network for as-indented PI a-Si may also be suggested by the absence of a significant number of atoms on the site of the first four-bonded atoms as indicated by the very small peak area observed.

7.4 Vibrational Properties

The SRO characteristics obtained by Raman microspectroscopy for magnetron-sputtered, ion-implanted and PI a-Si are presented below. Not only was the bond-angle distortion determined, but also significant insight into order on the length-scale of \(\sim 4-6\ \AA\) was obtained. Raman spectra from these purely amorphous films are presented in Fig. 7.6. In all cases spectra for the as-prepared and annealed films are shown with the former labelled as (1) and the latter labelled as (2) (in red). Each annealed/relaxed spectrum is offset for clarity.

The results for the magnetron-sputtered films deposited at room temperature and at 300°C are shown in Fig. 7.6(a) and (b), respectively. Clearly, in all sputtered cases the Raman laser penetrates through the a-Si layer and samples the crystalline substrate. Interestingly however, despite the same nominal film thickness the intensity of the c-Si TO band and thus volume of the c-Si sampled by the laser differs for all cases. Both room temperature films exhibit a larger intensity of the c-Si TO band than the films sputtered at 300°C. In both deposition cases, however, annealing increases this intensity. The first effect is possibly due to a lower mass density and thus higher void/nanopore density of the room temperature film. This lower mass density would allow an increased penetration depth of the Raman laser and thus an increased intensity of the bands originating from the substrate. The latter effect could be due to a decrease in film thickness upon annealing. This has been observed for the 300°C deposition and presumably also occurs in the room temperature case. A thickness decrease of \(\sim 2\%\) as observed for the 300°C case could well account for the slightly increased intensity of the c-Si TO band.

In the bottom row of Fig. 7.6, the spectra from as-prepared and relaxed pure a-Si are shown, ion-implanted in (c) and PI in (d). In the ion-implanted case no influence

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\(^b\)See Fig. 4.4 and Table 4.1 for details.
Section 7.4: Vibrational Properties

Figure 7.6: Raman spectra of sputtered a-Si deposited (a) at room temperature and (b) at 300°C, of (c) ion-implanted a-Si and of (d) PI a-Si. In each case spectra (1) is taken from the as-prepared film (in black) and spectra (2) from the annealed/relaxed film (in red). The latter spectra are offset for clarity.

of the substrate is observed as the film thickness of \( \sim 2 \, \mu m \) is considerably larger than the penetration depth of the laser. In the case of the PI a-Si however, a contribution of the underlying c-Si can be observed. Although less prominent in the relaxed PI case, in the as-implanted PI case the c-Si TO band is clearly split into two bands at 510 cm\(^{-1}\) and 528 cm\(^{-1}\). This behaviour is presumed to be due to residual stresses in the underlying c-Si introduced by the indentation. The band at 510 cm\(^{-1}\) is consistent with tensile stress, whereas the band at 528 cm\(^{-1}\) is suggestive of compressive stress [101, 223, 224]. The reason for the presence of two distinct bands rather than an integration over the entire c-Si volume sampled might be due to the fact that residual stresses are directional. Therefore, it is likely that the tensile stress present in the underlying c-Si is in the x/y-direction of the indenter geometry and thus a precursor to the formation of a median crack [225], whereas the compressive stress in the underlying c-Si is in the z-direction of the indenter geometry and appears insufficiently high to initiate phase transformation.

Interestingly, even from visual comparison of the spectra significant differences after
annealing can be observed between the sputtered and pure films. While the area under the TO-like peak seems only slightly increased for annealed sputtered a-Si when compared to as-sputtered a-Si (taking the offset added for clarity into account), the area seems significantly increased for the relaxed pure films when compared to their as-prepared counterparts. Furthermore, the peaks appear narrower after annealing in the latter cases indicating a decrease of $\Gamma_{TO}/2$. This behaviour is investigated in detail by determination of $\omega_{TO}$, $\Gamma_{TO}/2$ (and thus $\Delta \theta$) and of the intensity ratio $I_{TA}/I_{TO}$. Five spectra were analysed per form of a-Si and the averaged values are presented together with the respective standard error in Table 7.3. Details of the exact analytical procedure were given in Section 2.2.1. Similar trends upon annealing can be observed for all cases as all forms of a-Si undergo some short-range ordering although to a different extent.

For the sputtered case, $\omega_{TO}$ shifts towards higher wavenumbers by up to $\sim 4$ cm$^{-1}$, accompanied by a decrease in $\Delta \theta$. In the case of the room temperature sputtered film, this decrease in $\Delta \theta$ is 1.5°, whereas the 300°C film only undergoes very subtle short-range ordering. Nonetheless, the room temperature film remains less ordered upon annealing than the 300°C film. This is different for the intensity ratio $I_{TA}/I_{TO}$ which is indicative of the IRO. On this length-scale both sputtered films undergo structural ordering to the same value.

For the pure ion-implanted and PI cases, $\omega_{TO}$ shifts by $\sim 7$ cm$^{-1}$ on relaxation and additionally $\Delta \theta$ is reduced by $\sim 2°$ to significantly under 10° suggesting the convergence to a CRN-like network. Modelling has suggested that for CRNs the lowest possible bond-angle distortion is 6.6° [29]. However a recent study [60] comparing the Raman spectra

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>$\omega_{TO}$ [cm$^{-1}$]</th>
<th>$\Gamma_{TO}/2$ [cm$^{-1}$]</th>
<th>$\Delta \theta$ [deg]</th>
<th>$I_{TA}/I_{TO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-sputt. RT</td>
<td>468.9±0.6</td>
<td>44.5±0.4</td>
<td>12.3±0.1</td>
<td>0.643±0.009</td>
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<tr>
<td>ann. sputt. RT</td>
<td>472.9±0.8</td>
<td>39.8±0.6</td>
<td>10.8±0.2</td>
<td>0.460±0.015</td>
</tr>
<tr>
<td>as-sputt. 300°C</td>
<td>473.8±0.5</td>
<td>39.0±0.5</td>
<td>10.5±0.2</td>
<td>0.501±0.003</td>
</tr>
<tr>
<td>ann. sputt. 300°C</td>
<td>475.7±0.1</td>
<td>37.8±0.3</td>
<td>10.1±0.1</td>
<td>0.454±0.003</td>
</tr>
<tr>
<td>as-implanted</td>
<td>470.6±0.4</td>
<td>39.8±0.4</td>
<td>10.8±0.1</td>
<td>0.636±0.019</td>
</tr>
<tr>
<td>relaxed implanted</td>
<td>477.8±0.2</td>
<td>34.7±0.3</td>
<td>9.1±0.1</td>
<td>0.395±0.006</td>
</tr>
<tr>
<td>as-indent. PI</td>
<td>472.8±0.1</td>
<td>42.0±0.2</td>
<td>11.5±0.1</td>
<td>0.744±0.008</td>
</tr>
<tr>
<td>relaxed PI</td>
<td>478.0±0.3</td>
<td>36.1±0.1</td>
<td>9.5±0.1</td>
<td>0.432±0.002</td>
</tr>
</tbody>
</table>

Table 7.3: Comparison of $\omega_{TO}$, $\Gamma_{TO}/2$, the calculated $\Delta \theta$ and $I_{TA}/I_{TO}$ for the different as-prepared and annealed forms of a-Si. The bond-angle distortion $\Delta \theta$ is calculated after Beeman et al. [29].
of various forms of a-Si with different thermal history revealed 9° as a limit for the lowest possible bond-angle distortion. This may indicate that relaxed a-Si in these pure cases has reached the most ordered state possible.

The ion-implanted and PI films also undergo significant ordering on the IRO to values below that of the sputtered films. It is also noteworthy that the intensity ratio of as-indented PI a-Si is the highest of all forms of a-Si studied. This indicates that as-indented PI a-Si is truly the least ordered of all a-Si forms studied here.

The trends observed here agree well with literature reports where a decrease in $\frac{\Gamma_{TO}}{2}$ of $\sim 8 \text{ cm}^{-1}$ has been observed upon annealing of ion-implanted a-Si [13, 28], together with a reduction of the intensity ratio from 0.54 to 0.37 [28]. For sputtered a-Si a large range of values has been observed across different studies. One study observed $\frac{\Gamma_{TO}}{2}$ to range from 45 cm$^{-1}$ to 75 cm$^{-1}$ with corresponding intensity ratios of 0.55 to 0.80 [31]. Another study, measured a $\frac{\Gamma_{TO}}{2}$ of 55 cm$^{-1}$ with a ratio of 0.50 [135]. However, care has to be taken when comparing these different studies as the order in sputtered a-Si was found to be depth dependent (with less order present in the near surface region) and hence the measurement is sensitive to the penetration depth of the laser employed [135, 136]. Nonetheless, these very different parameters, especially for $\frac{\Gamma_{TO}}{2}$, do indicate how sensitive the order of the resulting amorphous network is to the exact deposition conditions.

Overall, the results obtained here from the vibrational properties examined by Raman microspectroscopy indicate that only the pure forms of a-Si, ion-implanted and PI, undergo structural relaxation to a CRN-like network. The sputtered films undergo some structural ordering, but do not approach the characteristics of a CRN as closely as the pure forms do.

### 7.5 Summary

Very interesting differences and also some similarities were observed between the various forms of a-Si, not only between as-prepared and relaxed, but also between one as-prepared form and another. In summary, all forms of a-Si undergo some short-range ordering upon annealing as indicated by the decrease in bond-angle distortion and the intensity ratio $I_{TA}/I_{TO}$. However, only the two pure forms appear to relax to a CRN-like network, whereas the bond-angle distortion of the annealed sputtered networks remains high. Such differences between the as-implanted and relaxed implanted network were not observed in the quantitative electron diffraction study. However, clear differences were observed for the as-indented and relaxed PI a-Si, with only the as-indented network being different to the other forms of a-Si.

The presence of heterogeneities and/or high MRO observed by FEM for the as-implanted cases is not replicated on the SRO/IRO length-scale. Instead less order than for
the relaxed cases is observed by Raman microspectroscopy and no significant differences to the relaxed cases is observed in the quantitative electron diffraction study. As-indented PI a-Si however, is clearly less ordered than any other form of a-Si on the SRO- and IRO-scale. This is evidenced from the very high $I_{TA}/I_{TO}$ ratio observed by Raman microspectroscopy as well as from the analysis of the RDFs and reduced RDFs. The electron diffraction data may suggest that the as-indented network departs from tetrahedral bonding which could account for this very low MRO observed by FEM. Thus, although Raman microspectroscopy and electron diffraction yield different structural properties on the same SRO-scale, both indicate that little order is present in as-indented PI a-Si, making the techniques complementary to each other.

To gain a full understanding of all these structural changes upon annealing and also structural differences in the as-prepared forms, a detailed comparison of these nearest-neighbour characteristics with the MRO as well as the mechanical properties is clearly needed. This will be performed in the next chapter.
Chapter 8

Framework for the Understanding of the Structure of Amorphous Silicon
In this work, a range of different forms of amorphous silicon has been investigated thoroughly using a variety of characterization techniques. As detailed in Chapter 3 the different forms of a-Si were prepared by all three principal methods of forming amorphous materials, namely vapour deposition techniques, quenching from the melt and solid-state amorphization. Specifically plasma-enhanced chemical vapour deposition (PECVD), magnetron-sputtering, quenching from a laser-induced melt, ion-implantation and a pressure-induced structural collapse were used. For all these different forms of a-Si the influence of thermal annealing and thus the ability of the network to structurally relax was examined.

These different forms of a-Si and their ‘relaxation’ annealed counterparts were first studied for their bulk properties such as impurity content, mass density, microstructure and also mechanical properties using conventional TEM, secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS), electron-energy-loss spectroscopy (EELS) and nanoindentation [see Chapters 4 and 5 for details]. The interest in the mechanical properties was twofold, with the deformation behaviour being clearly sensitive to the ‘state’ of the network and the indentation hardness susceptible to more subtle differences in network structure.

The more uniform a-Si films were then studied for their structural properties in detail. The techniques used for the structural characterization were quantitative electron diffraction and Raman microspectroscopy to investigate the short-range order (SRO) and intermediate-range order (IRO) [see Chapter 7 for details] and fluctuation electron microscopy (FEM) to investigate the medium-range order (MRO) [see Chapter 6 for details].

These properties will now be utilized with the aim of creating a general framework for the understanding of the structure of amorphous silicon. Such a framework is important as a first step towards more realistic models since without detailed experimental data no assertive validation of any model is possible. However, with a framework in place ab initio and/or variations of reverse Monte-Carlo (RMC) modelling will be necessary to establish a detailed understanding of the structure of a-Si.

Modelling of a-Si has only had limited success to date since no model exists that adequately replicates all experimental data [33]. Many ab initio models such as the WWW-models or models generated by molecular-dynamics (MD) tend to overestimate the coordination number (see, for example, [35] for the former and [36–39] for the latter case). Even MD models taking the formation method into account and, for example, simulating an amorphous structure formed by ion-irradiation, obtain such an overestimated coordination number [211]. Furthermore, to date RMC modelling to diffraction data has struggled with too little constraint on the solution space, resulting in many possible structures satisfying the experimental data [43, 44]. Modelling of FEM data by simulation of the FEM signal from proposed models [147, 151, 152] or by experimentally constrained molecular relaxation [53] suffers from similar problems, namely the essential ‘non-uniqueness’ of such models. Two different models have been found to date which fit the experimental
Section 8.1: Summary of Bulk Characteristics

data of a-Si equally well: a model based on voids [53, 54] and a model based on the
presence of paracrystals [15, 48–51]. This suggests that models simulated to fit FEM data
need to be very carefully scrutinized and compared for consistency with other available
data.

However, lack of available experimental data can impede conclusive modelling some-
what. For example, in the FEM data the scale of the decrease in peak magnitude of ion-
implanted a-Si upon relaxation appears different when measured by the tilted dark-field or
the STEM-FEM method. In addition, STEM-FEM observes two distinct groups with dif-
ferent variance, and hence MRO, for the as-implanted case. Thus, it will be challenging
to incorporate such apparent discrepancies into the modelling procedure. Nonetheless,
this study has provided significant new results and insight into the structure of a-Si and
will thus hopefully lead to further results that can be used to validate ab initio models,
for example, against the FEM and SRO data or by including FEM data into variations of
RMC modelling.

In this chapter the bulk properties will first be briefly summarized. Thereafter, the
structural order of the various forms of a-Si over the whole length-scale from 0 to \(\sim 3\) nm
studied (i.e. SRO, IRO, MRO) will be compared. Finally, the insights gained into the
structure of the specific forms of a-Si will be discussed in some depth.

8.1 Summary of Bulk Characteristics

The forms of a-Si made from bulk c-Si (i.e. laser-quenched, ion-implanted and PI) are
expected to all have the same impurity content, namely under 0.02 at.% as determined
by SIMS. In contrast, the deposited films (PECVD and magnetron-sputtering) have a
considerably higher total impurity content with \(\sim 20\) at.% in the case of the PECVD film
and \(\sim 5\) at.% in the case of the magnetron-sputtered films. In these sputtered cases the
impurities consist not only of H and O, but additionally of \(\sim 2\) at.% Ar included as residual
gas within the network.

While the sputtered and PI a-Si appear reasonably uniform, the PECVD and laser-
quenched a-Si are clearly not. Both these films contain a significant volume fraction of
crystallites, with the laser-quenched a-Si also containing a large void fraction. Moreover,
the high H content of the PECVD film results in a network more closely resembling the
alloy a-Si\(_{1-x}\)H\(_x\) than a true a-Si network. Therefore, these non-uniform forms of a-Si
were not investigated for the structural properties although their deformation behaviour
(and thus ability to relax) was examined.

A key result of this work is that after annealing only the uniform, pure forms of a-Si
(ion-implanted and PI) were found to readily phase transform upon indentation testing.
This indicates that only these forms of a-Si undergo structural relaxation upon thermal
annealing. No evidence of phase transformation was observed for any of the other films
Table 8.1: Summary of the uniformity, impurity contents and the influence of thermal annealing on the various forms of a-Si.

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>Uniformity</th>
<th>Total Impurity Content</th>
<th>State after Relaxation Anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECVD</td>
<td>crystallites</td>
<td>~ $10^{21}$ cm$^{-3}$</td>
<td>unrelaxed</td>
</tr>
<tr>
<td>laser-quenched</td>
<td>crystallites and voids</td>
<td>$\leq 10^{19}$ cm$^{-3}$</td>
<td>unrelaxed</td>
</tr>
<tr>
<td>sputtered RT</td>
<td>microstructure$^a$</td>
<td>~ $10^{20}$ cm$^{-3}$</td>
<td>unrelaxed</td>
</tr>
<tr>
<td>sputtered 300°C</td>
<td>microstructure</td>
<td>~ $10^{20}$ cm$^{-3}$</td>
<td>unrelaxed</td>
</tr>
<tr>
<td>ion-implanted</td>
<td>uniform</td>
<td>$\leq 10^{19}$ cm$^{-3}$</td>
<td>relaxed</td>
</tr>
<tr>
<td>pressure-induced</td>
<td>uniform</td>
<td>$\leq 10^{19}$ cm$^{-3}$</td>
<td>relaxed</td>
</tr>
</tbody>
</table>

$^a$This film had not been examined for its uniformity and impurity content in depth and thus may be even less uniform than the 300°C film as suggested by its lower indentation hardness although its impurity content is expected to be similar.

before and after annealing. This suggest that these forms of a-Si appear to remain ‘unrelaxed’ even after annealing.

The more uniform forms of a-Si (magnetron-sputtered, ion-implanted and PI) were also investigated for their mass density. All of them with the exception of as-indented PI a-Si were found to be less dense than c-Si. For the sputtered cases, this density-deficit of ~5% presumably results from microstructure such as nanopores which can be clearly observed by TEM imaging. The mass density of ion-implanted a-Si was found to be ~2% less than c-Si consistent with previous studies [23]. The increased mass density of as-indented PI a-Si is also accompanied by its significantly increased indentation hardness when compared to c-Si. Interestingly, for all other forms of a-Si, the indentation hardness was decreased when compared to c-Si.

The observations for all the different forms of a-Si obtained for their uniformity (from XTEM), impurity content (from RBS and SIMS) and state after thermal annealing (from indentation) are summarized in Table 8.1.

8.2 Structural Characteristics Relative to Relaxed Networks

For the more uniform forms of a-Si (magnetron-sputtered, ion-implanted and PI) the structural order was thoroughly investigated$^a$. Quantitative information was limited to

$^a$Note that, in the case of the sputtered a-Si, only the film deposited at elevated temperatures was investigated for its MRO characteristics as only this film etched to a sufficiently uniform TEM specimen.
Section 8.2: Structural Characteristics Relative to Relaxed Networks

SRO characteristics such as the bond-angle distortion obtained by Raman microspectroscopy and the coordination numbers (CN) obtained by electron diffraction. The information about the MRO obtained by FEM as well as information about the IRO by Raman microspectroscopy is qualitative only but is useful for comparison purposes and for expressing trends. Much of the information accessed by electron diffraction can only provide qualitative trends: for example, it can only be concluded that as-indented PI a-Si is less ordered than the other networks. Nonetheless, these trends can give insights into the structural properties of amorphous networks.

Ideally it is desirable to compare these trends by normalization to a CRN or at least a CRN-like network. An ideal a-Si CRN is expected to have full four-fold coordination as its only specific structural feature [10] with a mass density higher than that of c-Si [35]. In addition, its bond-angle distortion may be as low as 6.6° as estimated from models [29]. Clearly, even relaxed implanted a-Si departs from this structure and is hence only CRN-like and not an ideal CRN. However, a recent, extensive Raman microspectroscopy study has revealed (experimentally) that no lower bond-angle distortion than 9° is possible. In combination with the other structural data such as the low MRO and IRO, this suggests that the relaxed implanted a-Si studied here is as close to an ideal CRN as experimentally possible despite its slight under-coordination and density-deficit. Hence, this CRN-like relaxed implanted network was used as a ‘standard’ and the structural deviations of the other networks from this CRN-like network were examined.

Such deviations from a CRN-like network are shown for ion-implanted, pressure-induced and magnetron-sputtered (300°C) a-Si in Fig. 8.1. The deviations from the CRN-like network on all three length-scales are shown in Fig. 8.1(a) and the SRO and IRO are shown again in more detail in Fig. 8.1(b). The SRO and IRO characteristics used were obtained from the bond-angle distortion and intensity ratio \(I_{TA}/I_{TO}\), respectively, both measured by Raman microspectroscopy. The MRO was obtained by FEM, the tilted dark-field method in the PI and implanted case and the STEM-FEM method in the sputtered and second implanted case. The magnitude of the first peak was used rather than the peak magnitude ratio as the latter is convoluted with roughness effects in the tilted dark-field method. The error presented in these figures is the propagating error from the measurement of the relaxed implanted a-Si and the respective form of a-Si.

Only the structural properties of relaxed PI a-Si are very close to these of relaxed implanted a-Si suggesting that PI a-Si had undergone structural relaxation to a similar CRN-like network. The properties of the other forms of a-Si, even of the annealed sputtered a-Si, are significantly different. Note that, although the uncertainty on the MRO-scale is rather large, none of the other forms of a-Si approach a CRN-like network on this scale. Intriguingly, all forms of a-Si are less ordered than a CRN-like network on the SRO- and IRO-scale, but not necessarily so on the MRO-scale. Indeed only as-indented a-Si is less ordered than a CRN-like network on the MRO-scale. In contrast, the as-implanted and
Figure 8.1: Deviation from the CRN-like relaxed implanted a-Si on (a) the SRO-, IRO- and MRO-scales and on (b) the SRO- and IRO-scales. The SRO is obtained from the bond-angle distortion $\Delta \theta$, the IRO from the Raman intensity ratio $I_{TA}/I_{TO}$ and the MRO from the magnitude of the first peak of the FEM data.

Both sputtered networks are more ordered on this scale suggesting the possible presence of inhomogeneities. Furthermore, while as-implanted and as-sputtered a-Si appear similar on the SRO- and MRO-scale, as-implanted a-Si is significantly less ordered on the IRO-scale. Therefore, this simple plot that considers the deviations from a CRN-like network clearly indicates that all as-prepared networks significantly differ from each other.

Thus, the combination of a variety of characterization techniques employed in this current work provides a unique insight into the structural properties of the different amorphous networks. These structural properties are discussed for each form of a-Si separately in the next three sections. Note that the influence of the relaxation anneal will be discussed with each form of a-Si as structural relaxation (or lack thereof) also gives insight into the structural properties of the network. However, before discussing this in some depth, a
comment on the role of hydrogen diffusion into pure a-Si during thermal annealing is warranted.

The Role of Hydrogen In-diffusion during Annealing

After the thermal anneal at 450°C the concentration of hydrogen in relaxed ion-implanted a-Si ranges from around $7 \times 10^{19}$ cm$^{-3}$ on the top surface to around $1 \times 10^{19}$ cm$^{-3}$ at a depth of 120 nm as measured by secondary ion mass spectrometry. The hydrogen concentration in as-implanted a-Si is below the sensitivity limit of the experimental set-up, but is presumed to be similar to the equilibrium concentration of hydrogen in c-Si of around $1 \times 10^{12}$ cm$^{-3}$ [212] since no in-diffusion is expected to occur at room temperature [226]. The concentrations will be the same for relaxed and as-indentent PI a-Si, respectively, as they are also created from c-Si and, in the case of relaxed PI a-Si, annealed in the same way. One might argue that this hydrogen in-diffusion might be responsible for the change in the amorphous network upon annealing rather than an intrinsic change of the structure. Indeed, a decrease of the variance intensity obtained from FEM has been reported for hydrogen diffusion into certain types of magnetron sputtered a-Si (Ref. [148] and references therein). These films however, contained around 15% hydrogen after the in-diffusion, a concentration that is not only much higher than the observed concentration in the films studied here, but even higher than the solubility limit of hydrogen in ion-implanted a-Si (3-4%) [227]. Additionally, no downshift in peak position was observed in this previous FEM study, which suggests a different change to the amorphous network than caused by thermal annealing. Moreover, a previous study [228] as well as this current study observed that (hydrogenated) PECVD grown a-Si will not phase transform but deform via plastic flow, even if polycrystalline. Thus, hydrogenated networks seem to be structurally different from the relaxed a-Si networks studied here as both relaxed forms of a-Si clearly phase transform. Therefore, the in-diffusion of hydrogen during annealing does not seem to play a significant role for the changes in the amorphous networks observed upon annealing.

The influence of annealing on the structural properties as well as the initial starting structure of the various forms of a-Si are now discussed in detail.

8.3 Structure of Sputtered Amorphous Silicon

In this work only films deposited at 300°C were investigated for their structural properties. As detailed in Chapter 3 the structural properties of a deposited film depend critically on the deposition condition. Therefore, it is very likely that films grown under different conditions will have different structural properties. Nonetheless, many of the properties such as impurity content as well as density-deficit of the samples used here are represen-
Chapter 8: The Structure of Amorphous Silicon

tative for a typical magnetron-sputtered a-Si film. Thus, the structural characterization of this film allows structural differences between sputtered and ion-implanted or pressure-induced a-Si to be assessed.

The a-Si film deposited at 300°C exhibits similar SRO characteristics as the as-implanted film although the IRO is slightly increased. Additionally, the degree of MRO appears similar with the magnitude of the first peak being the same for as-implanted and as-sputtered a-Si. A previous study has observed a similar degree of MRO for as-sputtered and as-implanted a-Si and assumed therefore a similar paracrystalline network for both cases [46]. However, this present study observed very significant differences in the FEM data for sputtered and implanted a-Si, namely different peak shapes and a different magnitude of the second peak resulting in a very different peak magnitude ratio. Moreover, as-implanted a-Si was clearly observed to be heterogeneous on a highly localized length-scale (as indicated by the groups of ‘high’ and ‘low’ variance in the STEM-FEM data) which was not observed for sputtered a-Si. Therefore, clearly sputtered and ion-implanted a-Si are fundamentally different in terms of structure.

Firstly, the nature of the order (i.e. the inhomogeneities) in this as-sputtered state will be considered. Previous studies have reported a paracrystalline network for sputtered a-Si [45, 50, 146]. This paracrystalline network had been inferred from the high degree of MRO, but also from peak shapes and peak magnitude ratios. In particular, the peak magnitude ratio has been shown to be very sensitive to the presence of paracrystallites and even their orientation, shape and size [151, 152]. For example, simulations of paracrystalline networks have shown that the peak magnitude ratio exceeds 0.9 and that an ideal CRN is expected to have a ratio of 0.7 [152]. In contrast, the as-sputtered network studied here displays a considerably lower peak magnitude ratio of \( \sim 0.5 \). Additionally, a distinct third peak at 0.61 Å\(^{-1}\) is ‘expected’ for paracrystalline networks [152], which may not be present in this case. This may suggest that the sputtered a-Si studied here is indeed fully amorphous and not paracrystalline.

Although direct construction of a unique structural model from FEM data is impossible, insight into the structural characteristics can be inferred from the other properties of the film. For example, the sputtered a-Si exhibits a density-deficit of \( \sim 5\% \) over c-Si as measured by RBS which can be attributed to the presence of nanopores. This is also indicated by the significant densification occurring under indentation testing. Moreover, the indentation hardness of as-sputtered a-Si is slightly increased over as-implanted a-Si which may be due to the defects present in the as-implanted case facilitating deformation via plastic flow more easily. The presence of this microstructure is not surprising as sputter-deposition is well known to result in gas inclusions and microstructural features such as columnar growth and porosity [168]. Therefore, the nature of the inhomogeneities giving rise to the high degree of MRO in the present work is tentatively attributed to such void-like and microstructural features that are a result of a low density. In support of this,
modelling of porous a-Si has revealed that the material between the pores is considerably more ordered than in a comparable non-porous (amorphous) material as the dangling bonds tend to be concentrated on the internal surfaces of the pores [18]. This observation might explain the higher IRO present in the as-sputtered a-Si as observed by the Raman microspectroscopy data when compared to the as-implanted case.

Interestingly, the changes to the network occurring upon thermal annealing are not as prominent as in the cases of ion-implanted or PI a-Si. A small change can be observed in the SRO and IRO. However, the inhomogeneities present in the network remain upon annealing as indicated by the unchanged high degree of MRO, although possibly a subtle shift in peak magnitude is observed in the FEM data. This indicates that although the network undergoes some short-range ordering the network does not appear to be able to relax to a homogeneous CRN-like network. Moreover, the persistence of the high degree of MRO might also suggest that the high variance measured in this sputtered sample is not due to paracrystallinity as paracrystals below 3 nm in size are known to collapse upon annealing to a disordered network [220]. Therefore the high MRO observed in the sputtered case even after ex-situ annealing is highly unlikely to be due to paracrystallinity. Also note that this increase in SRO upon annealing of the sputtered film as observed by Raman microspectroscopy is not due to hydrogen as a decrease in H content (as observed upon ex situ annealing) will result in a decrease in SRO rather than in an increase [60, 178]. Furthermore, the density-deficit observed for the as-sputtered case remains, although the mechanical properties change somewhat as indicated by an increased indentation hardness. Interestingly, the annealed film also deforms via plastic flow/compression rather than via a phase transformation. This indicates strongly that the film did not structurally relax and no CRN-like network had been formed upon annealing.

There are two possibilities for the inability of sputtered films to relax: either as a result of the impurities or the microstructure. Although the total H and O concentration is \( \sim 2 \) at.\%, it seems unlikely that this would completely prohibit phase transformation from occurring. Firstly, indentation studies of ion-implanted a-Si enriched with H and O content at the same level found phase transformation to the crystalline high-pressure phases to be still possible although retarded [229, 230]. Secondly, other indentation studies of magnetron-sputtered a-Si have observed phase transformation to these crystalline phases in some cases, but the structural details of the films were not given [109]. Indeed, this ‘random’ occurrence of phase transformation reported in Ref. [109] seems rather similar to the retardation effect (for H and O) observed in the ion-implantation studies. The lack of phase transformation in the present case, despite extensive attempts, may thus suggest that the inability to relax is due to the presence of nanopores and voids. Such microscopic nanopores/voids on the MRO-scale may inhibit atomic rearrangement necessary for complete relaxation and convergence to a CRN-like network. As a result the observed small changes on the SRO- as well as MRO-scale upon annealing could well be due to homog-
enization of the material between the pores. Thus, the sputtered network may undergo structural ordering on a small scale, but cannot do so on a sufficiently large scale. Therefore, it remains essentially in its original inhomogeneous form which is clearly reflected in its MRO characteristics and also in the lack of phase transformation. Interestingly, this result implies that it might well be possible to structurally relax and then phase transform a sputtered film if it is deposited under conditions preventing the formation of such microstructure while simultaneously ensuring higher purity.

8.4 Structure of Ion-Implanted Amorphous Silicon

Although ion-implanted a-Si is the form of a-Si with the most previous studies performed on its structure and its mechanism for structural relaxation, significant new insights have been gained by this current work. Previous studies have shown that, upon annealing, the network undergoes ordering on the SRO as well as IRO length-scales [13, 28], whereas the MRO was previously reported to decrease [46, 55]. This structural relaxation has been quantified by X-ray diffraction which detected a small increase in coordination number upon annealing although even the relaxed network remained slightly under-coordinated [14]. As both the as-implanted and relaxed networks possess a density-deficit of $\sim 2\%$ when compared to c-Si [23] previous studies interpreted structural relaxation as defect annihilation in terms of a point-defect/interstitial recombination [13, 14]. In fact, the reduction in dangling-bond density has been confirmed by positron annihilation [61]. These structural changes are also represented in the mechanical properties with as-implanted a-Si being considerably softer than c-Si, whereas annealing increases this indentation hardness [20]. Additionally, relaxed implanted a-Si was observed to deform via a phase transformation whereas as-implanted a-Si will deform via plastic flow [21, 22].

In this present work these previous observations have been largely replicated. Namely, upon annealing the same short-range and intermediate-range ordering was observed by Raman microspectroscopy from the reduction in bond-angle distortion and intensity ratio. In addition, the density-deficit of $\sim 2\%$ was confirmed using EELS and the undercoordination using quantitative electron diffraction. Lastly, a similar decrease of order on the MRO-scale as reported in previous studies was observed.

In addition to the confirmation of these previous results some improvements in techniques such as FEM have yielded new insights into the structure of as-implanted a-Si. For example, in addition to the decrease of MRO indicated by the reduction in peak magnitude a subtle down-shift of the variance peak positions was observed upon annealing. This down-shift of peak positions can be attributed to the changes in the local bonding and thus to the short-range ordering observed. Furthermore, a very low variance peak magnitude ratio was obtained from the STEM-FEM data for as-implanted as well as relaxed implanted a-Si. This low ratio for ion-implanted a-Si is inconsistent with models
of paracrystalline structure [151, 152] and suggests alternative structures on this length-scale. Indeed, STEM-FEM observed the clear presence of heterogeneities within the as-implanted network as indicated by two different groups of areas with ‘high’ and ‘low’ variance. Therefore, although many of the properties of ion-implanted a-Si had already been determined prior to this study, some new information relating to its structure and the mechanism behind structural relaxation has been obtained.

Firstly, the structure of the as-implanted network is regarded as a defective CRN with a large number of defects and defect complexes such as dangling bonds, interstitials and bonding defects (see Ref. [188] and references therein). This view is supported by the increased SRO and IRO upon annealing as well as the decreased dangling bond density resulting in an increased coordination number [14]. Moreover, this high defect or dangling bond density may aid material flow by facilitating propagation of defects or dangling bonds thus explaining the low indentation hardness and lack of phase transformation observed for the as-implanted case [21].

The high MRO observed by FEM however, does not entirely fit into this picture of a defective network with low order, but seems indicative of the presence of some inhomogeneities giving rise to this high MRO. The presence of such inhomogeneities seems confirmed by the two distinct groups of ‘high’ and ‘low’ variance in the STEM-FEM data. The nature of the order however, is not easy to ascertain resulting from the difficulty in interpreting MRO data obtained from FEM. A previous FEM study on as-implanted a-Si and the influence of thermal annealing on its network proposed the paracrystalline model for the as-implanted case with only the relaxed case being CRN-like [46, 55]. However, as detailed in Section 1.2 in the first chapter, there is some doubt about the amorphous nature of the specimen studied in this previous work.

To gain further insights into the high MRO observed for as-implanted a-Si it is worth considering how the implantation process itself might contribute to speckles in dark-field images or nanodiffraction patterns indicative of inhomogeneities on the MRO-scale. Ion-implanted a-Si and the disordering that leads to it arises from the sum of individual collision cascades caused by the implanted energetic Si ions [164, 188], a process which can clearly result in an inhomogeneous amorphous network. For example, within a collision cascade, the atomic motion can be considered as a displacement cascade or thermal spike. In the latter case local melting and quenching can occur on a time scale of the order of $10^{-15}$ s. Both types of collision spike can lead to bonding defects such as the IV defect and density variations across the cascade. Furthermore, the length-scale of the damage surrounding such a Si-ion collision cascade is slightly larger or of the order of the length-scale of the MRO probed here (1.2 nm in the tilted dark-field case). Thus, FEM is very likely to be sensitive to the inhomogeneities in a-Si generated by collisional processes of ion-implantation. Indeed, these cascade-induced local differences in structure may well be the inhomogeneities (or heterogeneities) which are being picked up by the STEM-FEM
method. Such inhomogeneities may consist, for example, of localized changes in mass density between the edges and the core of the cascades, ‘defect-like’ differences or differences in residual strain. ‘Defect-like’ differences could be differences in the ratio of the five- and seven-membered rings [34, 35] within the amorphous network at different parts of the residual cascade volumes. Such locally heterogeneous regions might have different atomic (bonding) arrangements and thus differences in local diffraction contrast might be expected to occur. These differences may appear as speckles on the dark-field image, yielding a larger intensity variance than a homogeneous medium of the same average density.

Possible new insights into the mechanism of the structural relaxation will be considered next. Clearly, the network undergoes short- and intermediate-range ordering as observed by Raman microspectroscopy. This structural relaxation has previously been linked to the annihilation of point-defects and point-defect complexes [13, 14, 64]. While these defect concentrations lead to a distortion of bond-angles and an accompanying strain field, their annihilation yields a more CRN-like network due to the reduction in the bond-angle distortion. In contrast, on the MRO-scale the order is decreased rather than increased and this decrease of MRO is accompanied by a downshift in the peak position and a small decrease of the peak magnitude ratio. Furthermore, the inhomogeneities observed by STEM-FEM for the as-implanted network disappear upon annealing. Also note that this decrease of MRO upon annealing was observed independently using the tilted dark-field method as well as the STEM-FEM method. Therefore, this structural re-ordering on the MRO-scale clearly suggests an homogenization of the amorphous network and thus the formation of a CRN-like network. In terms of structural relaxation, the findings presented in this study are entirely consistent with a defect annihilation model for relaxation if the homogenization of the network on the MRO-scale is additionally taken into account. Therefore, structural relaxation may well be a result of point-defect/interstitial recombination resulting in the increased SRO and IRO as well as removal of the inhomogeneities. This homogenization may be, for example, removal of IV pairs, which are known to be thermally unstable [188], or alternatively homogenization of local density differences.

Therefore, it is clear that ion-implanted a-Si relaxes to a network as close to a CRN as experimentally possible. This is also observed for the PI case and the structure of this other pure form of a-Si will be discussed in the next section.

### 8.5 Structure of Pressure-Induced Amorphous Silicon

To date, very little is known about the structural properties of PI a-Si and thus this present work gives a first insight into this unique form of a-Si. Intriguingly, PI a-Si was found to be significantly different from as-implanted a-Si although both networks are formed by solid-state amorphization and both relax to a CRN-like network upon annealing.
As-indented PI a-Si was found to have the lowest SRO and IRO of any amorphous network as observed by Raman microspectroscopy. In addition, a similar under-coordination as observed for ion-implanted a-Si was obtained from the radial distribution function. Moreover, the electron diffraction results suggest a lower order of this network than observed for any other form of a-Si as indicated by increased peak width in the RDF as well as reduced RDF and also the very low number of four-bond atoms. Furthermore, the lowest MRO of all forms of a-Si was measured by FEM and in fact, as-indented PI a-Si is the only network with a MRO lower than observed for a CRN-like network. This very low structural order on the entire length-scale is accompanied by a high mass density similar to the mass density of c-Si or possibly even higher. In turn, this high mass density gives rise to a higher indentation hardness than observed for even c-Si, although deformation still occurs via plastic flow.

The high density appears to be a result of its formation from the dense metallic Si-II phase, making the formation of PI a-Si fundamentally different from the formation of ion-implanted a-Si. In the latter case the a-Si forms by either sufficient accumulation of defects or by the overlap of amorphous pockets. In the PI case however, the long-range order of the crystalline Si-II is lost due to rapid unloading. This implies that the process is somewhat akin to a glass transition as the PI a-Si does not nucleate, but is formed by a collapse due to lattice instability. In fact, this is somewhat similar to the amorphization of ice from ice Ih at high pressures and low temperatures which is attributed to a structural collapse [203]. However, note that this amorphous ice had been found to be unrelaxed high-density amorphous (HDA) ice, whereas PI a-Si is a low-density amorphous form of silicon despite its relative high mass density\(^a\).

Therefore, the high mass density itself can give direct insight into the structural properties of PI a-Si, especially when considered in conjunction with the electron diffraction results. The increased width of the first peak of the RDF suggests a larger spread in bond-length than observed for the other amorphous networks. In addition, the significantly smaller peak height to peak width ratio observed in the reduced RDFs also points towards a larger spread in nearest-neighbour distances. However, the high mass density implies that equally many (or even more) atoms are present as in the other networks. Hence some atoms are clearly not represented in the reduced RDF (as also indicated by the smaller peak areas) which may imply that some atoms sit on non-tetrahedral sites and therefore yield a uniform background over the entire length-scale of the reduced RDF. Such a lack of a well formed tetrahedral network may also result in a reduced ‘speckliness’ in dark-field images and hence a measured low variance in the FEM data. Furthermore, the possible presence of such non-tetrahedrally bonded atoms may explain how it is possible for this network to possess less MRO than a CRN-like network. Whereas in the ion-implanted case vacancies and interstitials occur in balance [14], the presence of such non-tetrahedral

\(^a\)Note that HDA silicon has a mean coordination number of 4.6 [106]
atoms may suggest an excess of interstitials in the PI case. However, it might be of interest to also perform STEM-FEM with its capability of filtering for roughness effects on this form of a-Si as it is not clear if similar inhomogeneities as in the ion-implanted case exist. In light of the large scatter observed in the tilted dark-field data however, it might be worthwhile to investigate whether this scatter is caused by, for example, differences in structure between the surface and bottom regions of the phase transformed zone or other inhomogeneities.

The possibility of such a non-tetrahedral network may also account for the behaviour upon annealing. Clearly, the PI network undergoes ordering on the SRO, IRO and MRO length-scales to the same order as observed for relaxed implanted a-Si and thus also converges to a CRN-like network. In contrast to the ion-implanted case (which does not change its density) the ordering results in an expansion of the dense as-indented network thus decreasing the mass density. This is accompanied by a decrease in indentation hardness again in contrast to ion-implanted a-Si (where the indentation hardness increases). Lastly, this relaxation annealed PI a-Si was found to phase transform upon indentation testing in the same manner as relaxed ion-implanted a-Si does. Therefore, at least to the sensitivity of the techniques used in this current work, relaxed PI a-Si is structurally very similar to relaxed implanted a-Si and therefore to a CRN-like network.

In the case of ion-implanted a-Si the lack of change in density upon annealing [23] is consistent with structural relaxation as occurring during local defect annihilation [13, 14, 64]. This is clearly different in the case of PI a-Si suggesting a somewhat different mechanism of structural relaxation. Upon relaxation the RDF and reduced RDF become indistinguishable from the data for both implanted networks indicating that the atoms are now bonded within a tetrahedral network. Therefore the atoms in the as-indented network that were on non-tetrahedral sites move to tetrahedral sites during the annealing process, which is consistent with the ordering observed on all length-scales studied. In addition this is also consistent with an expansion (i.e. decrease in mass density) of the network resulting in the formation of a more open tetrahedral, CRN-like network.

This different structural relaxation mechanism together with the very different structural properties of as-indented PI a-Si clearly indicates the importance of the formation method on the resulting structure. Even more intriguing however, is the observation that both these pure amorphous films relax to a network which is as close to a CRN as appears experimentally possible.

8.6 Conclusions

In conclusion, each as-prepared form of a-Si was found to have very different structural properties. This results not only in differences in structural order, but also in different mass density. The sputtered a-Si contains microstructure in the form of nanopores and
voids. In this case dangling bonds will concentrate around the internal surfaces with the matter between the pores being more ordered than an as-implanted network [18]. In the pure ion-implanted case however, the a-Si is more uniform without significant microstructure, but instead contains a large number of defects such as dangling bonds, interstitials and bonding defects, often agglomerated in defect clusters. Additionally, inhomogeneities are present on the MRO-scale which give rise to a high MRO. Interestingly, in the case of PI a-Si the high mass density of this form of a-Si results in a slightly non-tetrahedral network with presumably many strained bonds. This clearly illustrates how influential the formation method is on the resulting structure.

Intriguingly, only the pure films without any microstructure, i.e. only the ion-implanted and PI a-Si, undergo structural relaxation upon thermal annealing. In the case of the sputtered a-Si the inhomogeneities in the form of nanopores/voids prevent the formation of a homogeneous network although small-scale short-range ordering was observed. In the pure a-Si cases, structural relaxation results in essentially the same structural properties on the SRO-, IRO- and MRO-scale as well as in the same phase transformation behaviour upon indentation testing. This structural relaxation can be attributed to, and is consistent with, defect annihilation in the implanted case and to the formation of a tetrahedral network in the PI case. This is indicated by the fact that in the case of the ion-implanted a-Si, removal of inhomogeneities, consisting of regions of correlated structure on the MRO-scale, takes place during structural relaxation, whereas in the PI case, the presumed removal of atoms from non-tetrahedral sites results in an expansion of the amorphous network. Nonetheless, both mechanisms of structural relaxation result in a homogeneous CRN-like network. This indicates that, regardless of the initial structure of the network, a-Si will tend to structurally relax to a network as close to a CRN as experimentally possible. However, the formation of a homogeneous CRN is only possible if not prevented by impurities or microstructure as in the sputtered case.

This absolute dependence of the resulting structure on the formation method may explain why \textit{ab initio} modelling of amorphous silicon has not been very successful to date. For example, it is clear that all as-prepared forms of a-Si differ significantly from a CRN or even CRN-like network, which should be taken into account for any future modelling. It might also be of interest to take the formation process of a particular form of a-Si (and its resulting properties) into account before modelling is started. This has been attempted to some degree for ion-implanted a-Si by MD simulations although many features such as the under-coordination and density-deficit cannot be replicated yet [188, 211]. Interestingly, PI a-Si might be closer to the more traditional MD approach of quenching the amorphous structure from the melt as liquid Si is somewhat similar to the metallic Si-II phase. The structure of PI a-Si may be somewhat consistent with the high mass density and large bond-angle distortion of up to 16° observed in some models [38, 62], but is inconsistent with the over-coordination observed for the same models.
Moreover, it might be of further interest to extend this framework to other tetrahedrally bonded amorphous semiconductors such as amorphous carbon and amorphous germanium. The structural properties of a-Ge might be of particular relevance as germanium is increasingly used as an electronic material. However, even less is known about the influence of the formation method on the a-Ge structure. For example, FEM has been performed on deposited a-Ge [47] but not in ion-implanted a-Ge. In addition, even its Raman characteristics are less well studied as many commercial Raman systems do not target good vibrational data below \( \sim 100 \text{ cm}^{-1} \) which needs to be accessed for the TA-like peak of a-Ge. However, in light of the large influence of the formation method on the structural properties of a-Si, such comparative, in-depth studies are clearly needed.
Chapter 9

Future Directions
In light of the development of a framework for the understanding of the structure of a-Si, the need for some further experimental work as well as for extensive modelling has become clear. More experimental studies will be of interest in order to answer some of the questions raised by this current work. More importantly, some of the knowledge gained by this current work may also be employed, for example, for the deposition of high-quality films of a-Si. Additionally, other experimental techniques outside of the scope of this work may elucidate further details of the structure of a-Si and also other amorphous semiconductors. Lastly, this current work can provide the stimulus for more realistic modelling of amorphous materials with the aim to fully understand their structure. This final chapter addresses some of these issues and makes some suggestions for future directions. Note that some of these suggested experiments are currently being performed, while many others will be conducted within the next year.

The first set of further experimental studies concerns the properties of PI a-Si. As mentioned in the previous chapter, it would be of great interest to perform STEM-FEM with its higher area sensitivity through correcting for non-uniform film thickness on this form of a-Si. This may elucidate whether structural order is uniform across the entire phase transformed zone or whether some inhomogeneities, as in the as-implanted case, exist. Furthermore, it would be advantageous to confirm the high mass density observed for PI a-Si and the observed decrease in mass density upon annealing by further means. For example, the mass density of as-indented and relaxed PI a-Si could also be measured by micro-RBS or by optical profilometry of residual indent impressions in order to obtain an independent confirmation of the values determined by EELS. In addition, many of its other characteristics such as, for example, its defect concentration remain unknown. Thus, it would be very illuminating to study the heat release during structural relaxation in situ by nanocalorimetry to compare it to the better characterized ion-implanted a-Si [66]. All these experiments would then aid in obtaining a full understanding of the structure of this entirely new form of a-Si.

Another important future direction lies in the further studies of laser-quenched a-Si. As clearly evident from Section 4.3.3 in Chapter 4, there is need for more uniform laser-quenched a-Si without voids and crystalline material if its structural properties are to be assessed. This would be very useful as laser-quenched a-Si is another pure form of a-Si and may therefore shed further light on the mechanism of structural relaxation from different starting forms.

As discussed in the previous chapter, ‘better’ deposited a-Si without microstructure and lower impurity content would be very beneficial. Since these characteristics seem to prevent the formation of a homogeneous CRN-like network, it seems likely that such deposited films may undergo structural relaxation upon annealing resulting in the ability to phase transform upon indentation testing. Such phase transformations in deposited films could be very useful for, for example, nanopatterning by indentation [231]. Therefore, the
characterization of a-Si deposited under ultra-high-vacuum conditions would be clearly of interest.

Furthermore, despite the extensive amount of studies already performed on the structure of ion-implanted a-Si, further work is clearly needed. Although the present work seems to indicate that the inhomogeneities observed in the as-implanted case are due to the implantation process itself, it would be beneficial to completely rule out that the high MRO observed is a remanent of its formation from the crystal, i.e. is due to the presence of paracrystals. This could be achieved by another FEM study on re-implanted, previously relaxed a-Si. As clearly relaxed a-Si is a CRN-like network re-implantation of such a film would eradicate the possibility of a 'memory effect'. The investigation of the inhomogeneities present in such a specimen would greatly elucidate the formation mechanism of ion-implanted a-Si.

Finally, the structure of other amorphous semiconductors such as a-Ge is also of great interest. As mentioned previously only one FEM study has been performed on a-Ge [47]. Therefore, it would be illuminating to investigate the influence of the formation of a-Ge on its structure by performing a comparative FEM and Raman microspectroscopy study on deposited and ion-implanted a-Ge. Such a study may also enable the extension of this present framework to other tetrahedrally bonded amorphous materials.

In addition to this suggested future experimental work, \textit{ab initio} modelling as well as variations of RMC modelling are essential for the full understanding of the structure of a-Si and other amorphous materials. Some suggestions for such modelling are presented now.

As has been discussed in previous chapters, the sole use of diffraction data for RMC modelling does not constrain the solution space sufficiently. However, the combination of diffraction data with FEM data adds further constraint to such modelling [232] thus improving the reliability of the resulting models. Therefore, such modelling would give great insight into the structure of the various forms of a-Si. In addition, it could be valuable to add information about vibrational properties as a further constraint during modelling or investigate the resulting models for consistency with the Raman data. Such modelling would clearly yield models closer to the actual physical structure.

In addition, most \textit{ab initio} models are only validated against experimental data for the SRO characteristics such as obtained from diffraction experiments and vibrational data. However, calculating the FEM signal from such models as generated by, for example, MD simulations could be a further validation mechanism for the reliability of such a model. In fact, it has been suggested that access to the MRO would be useful for such validation [38], but no experimental data were available at the time of the study.

In summary, these suggested future directions for experimental as well as modelling work may aid in obtaining a full understanding of the structure of a-Si and possibly also of other amorphous semiconductors.
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Appendix A

Details of the Structure of the Crystalline High-Pressure Phases of Silicon
In this appendix further details on the high-pressure phases of silicon will be given. In the first section the crystalline structure of the various phases forming upon loading and unloading will be summarized. In the second section the $d$-spacings and Raman bands of the silicon phases observed at ambient will be given. In the last section details of the proposed new phase of silicon, Si-XIII, will be presented.

### A.1 Silicon Phases upon Pressurization and Depressurization in Diamond-Anvil Cells

As has been detailed in Section 1.3.1 in the first chapter, twelve crystalline phases of silicon have been identified to date. The space group and crystalline structure of the phases forming upon loading in diamond-anvil cells are summarized in Table A.1, whereas the phases forming upon unloading are presented in Table A.2. For more details on these various crystalline phases refer to Refs. [67, 76] and references therein.

### A.2 Crystalline Silicon Phases (Meta-)Stable at Ambient

Although possibly six crystalline phases of silicon can be observed at ambient (i.e. Si-I, Si-III, Si-IV, Si-VIII, Si-IX and Si-XII), only four of these have been characterized in detail. These are the diamond cubic Si-I with $a = 5.43$ Å [157], the body-centred cubic Si-III with $a = 6.64$ Å [77], the hexagonal diamond Si-IV with $a = 3.80$ Å and $c = 6.28$ Å [77] and lastly the rhombohedral Si-XII with $a = 5.609$ Å and $\gamma = 110.07$ [81]. From these unit cells the $d$-spacings were calculated and are summarized in Table A.3. These $d$-spacings can then be used to identify the phases present within a phase transformed zone.

Note that SADPs from these phases within phase transformed zones are not usually indexed for two reasons: firstly, the crystallites observed in such phase transformed zones are very small (∼5-30 nm) which prohibits tracking one single crystal when tilting from one zone axis to another; secondly, these crystalline high-pressure phases are metastable which results in their annealing out to Si-I under the electron beam. This further complicates tilting from one zone axis to another. Thus, in general SADPs of these crystalline high-pressure phases only allow for measuring of the $d$-spacings. As many of these $d$-spacings can correspond to multiple phases and usually a mix of phases is expected within a phase transformed zone, it is not possible to index the diffraction patterns unambiguously. Therefore, only the measured $d$-spacings are marked in such SADPs. Also note that the error associated with measurement of the $d$-spacing is up to ±0.1 Å.

In addition to the structural properties, the vibrational properties of these phases can be examined using Raman microspectroscopy as all these phases are Raman active. The
# High-Pressure Phases of Silicon

<table>
<thead>
<tr>
<th>Pressure Regime [GPa]</th>
<th>Phase Label</th>
<th>Space Group</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-11.7</td>
<td>Si-I</td>
<td>(Fd\bar{3}m)</td>
<td>diamond cubic (dc)</td>
</tr>
<tr>
<td>11.7-13.2</td>
<td>Si-II</td>
<td>(I4_1/amd)</td>
<td>body-centred tetragonal ((\beta)-Sn)</td>
</tr>
<tr>
<td>13.2-15.4</td>
<td>Si-XI</td>
<td>(Imma)</td>
<td>body-centred orthorhombic</td>
</tr>
<tr>
<td>15.4-38</td>
<td>Si-V</td>
<td>(P6/mmm)</td>
<td>simple hexagonal</td>
</tr>
<tr>
<td>38-42</td>
<td>Si-VI</td>
<td>(Cmca)</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>42-79</td>
<td>Si-VII</td>
<td>(P6_3/mmm)</td>
<td>hexagonal close-packed</td>
</tr>
<tr>
<td>79-248</td>
<td>Si-X</td>
<td>(Fm\bar{3}m)</td>
<td>face-centred cubic</td>
</tr>
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</table>

Table A.1: High-pressure phases of Si upon loading.

<table>
<thead>
<tr>
<th>Pressure Regime [GPa]</th>
<th>Phase Label</th>
<th>Space Group</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-0</td>
<td>Si-XII</td>
<td>(R\bar{3})</td>
<td>rhombohedral (r8)</td>
</tr>
<tr>
<td>3.2-0</td>
<td>Si-III</td>
<td>(Ia\bar{3})</td>
<td>body-centred cubic (bc8)</td>
</tr>
<tr>
<td>-</td>
<td>Si-IV(^a)</td>
<td>(P6_3/mmc)</td>
<td>hexagonal diamond (hd)</td>
</tr>
<tr>
<td>14.8-0</td>
<td>Si-VIII(^b)</td>
<td>-</td>
<td>tetragonal</td>
</tr>
<tr>
<td>12-0</td>
<td>Si-IX(^b)</td>
<td>-</td>
<td>tetragonal</td>
</tr>
</tbody>
</table>

Table A.2: High-pressure phases of Si upon unloading.

\(^a\)This phase is obtained after moderate annealing (\(~200^\circ\)C) of Si-III [78].

\(^b\)These two phases were obtained after rapid depressurization from a metallic phase by Zhao et al. [233], but their structure remains unresolved.

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>111</td>
<td>3.14</td>
<td>110</td>
<td>4.70</td>
<td>100</td>
<td>3.29</td>
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<td>100</td>
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<td>101</td>
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<td>3.21</td>
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<td>220</td>
<td>2.35</td>
<td>102</td>
<td>2.27</td>
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<td>321</td>
<td>1.77</td>
<td>103</td>
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<td>2.57</td>
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<tr>
<td>511</td>
<td>1.05</td>
<td>400</td>
<td>1.66</td>
<td>200</td>
<td>1.65</td>
<td>11-3</td>
<td>1.87</td>
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</table>

Table A.3: List of the \(d\)-spacings of the various crystalline Si phases (meta-)stable at ambient temperature and pressure.
Appendix A

<table>
<thead>
<tr>
<th>Raman Band [cm(^{-1})]</th>
<th>Phase Label</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>166</td>
<td>Si-XII</td>
<td>r8</td>
</tr>
<tr>
<td>184</td>
<td>Si-III</td>
<td>bc8</td>
</tr>
<tr>
<td>300</td>
<td>Si-I (2TA)</td>
<td>dc</td>
</tr>
<tr>
<td>354</td>
<td>Si-XII</td>
<td>r8</td>
</tr>
<tr>
<td>377</td>
<td>Si-III/Si-XII</td>
<td>bc8/r8</td>
</tr>
<tr>
<td>386</td>
<td>Si-III</td>
<td>bc8</td>
</tr>
<tr>
<td>399</td>
<td>Si-XII</td>
<td>r8</td>
</tr>
<tr>
<td>412(^a)</td>
<td>Si-III</td>
<td>bc8</td>
</tr>
<tr>
<td>440</td>
<td>Si-III</td>
<td>bc8</td>
</tr>
<tr>
<td>(~470)</td>
<td>a-Si</td>
<td>amorphous</td>
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<tr>
<td>(~500-520)</td>
<td>Si-IV</td>
<td>hd</td>
</tr>
<tr>
<td>521</td>
<td>Si-I (TO)</td>
<td>dc</td>
</tr>
</tbody>
</table>

Table A.4: Raman bands of the different phases of silicon observed at ambient.

\(^a\)This Raman band has not been observed for the large spherical indent impressions used in this study, but only for indents prepared with pointed tips [95].

resulting wavenumbers, or Raman bands, observed for these phases are summarized in Table A.4. As the exact position of Raman band is highly pressure-dependent [130], the Raman bands presented here are, when possible, as measured for large-spherical indents made in c-Si [130].

The majority of the bands are labelled according to Ref. [101]. For some bands however, the labelling is less clear. For example, the bands at 166 cm\(^{-1}\) and 184 cm\(^{-1}\) have not previously been labelled. However, theoretical calculations of the vibrational properties of Si-III predict a band at 181 cm\(^{-1}\) [234] and hence the band observed at 184 cm\(^{-1}\) is labelled such. No further band is predicted for Si-III below 200 cm\(^{-1}\) and thus the band at 166 cm\(^{-1}\) is labelled as Si-XII. In the case of Si-IV, two Raman bands are theoretically expected [235]. The exact position of these bands however, seems to be somewhat dependent on the laser power used [235] and therefore the entire range possible for Si-IV bands is quoted in the table.

A.3 Thermal Annealing of High-Pressure Phase Indents

In addition to these known and identified phases recently the existence of a new crystalline phase of silicon has been proposed: the phase Si-XIII. This phase was first observed by the appearance of previously unreported Raman bands upon thermal annealing at 200°C of residual indent impressions prepared with pointed tips [103, 236]. In addition, our previous work on large-scale spherical indents prepared in c-Si as well as relaxed ion-implanted a-Si also reported these extra Raman bands forming upon annealing at 200°C [130]. In this previous study, first evidence of these extra Raman bands is observed after 5 minutes annealing and the bands remained throughout multiple days of annealing at this
High-Pressure Phases of Silicon

<table>
<thead>
<tr>
<th>Raman Band</th>
<th>Phase Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>202</td>
<td>Si-XIII</td>
</tr>
<tr>
<td>333</td>
<td>Si-XIII</td>
</tr>
<tr>
<td>478</td>
<td>Si-XIII</td>
</tr>
<tr>
<td>500</td>
<td>Si-XIII or Si-IV</td>
</tr>
</tbody>
</table>

Table A.5: Raman bands appearing after thermal annealing of Si-III/Si-XII formed beneath residual indent impressions.

Although detailed structural data allowing the identification of the space group are still lacking, electron diffraction performed on residual indent impressions has revealed further insight into this new phase. Therefore, large-scale spherical indentations of c-Si were prepared with the UMIS using the ∼18 µm tip loading up to 750 mN. The residual indent impressions were annealed at 200°C for 2.5 h as Raman microspectroscopy has revealed a large amount of Si-XIII under these conditions. The residual indents were examined in cross-sectional as well as plan-view geometry. SADPs taken from such residual indent impressions are shown in Fig. A.1 with the SAPD from the plan-view specimen shown in part (a) and from the cross-section in part (b).

As marked in the SADPs several new \(d\)-spacings can be observed which cannot be correlated to any of the known phases of silicon. Namely, these are \(d\)-spacings at 5.6 Å, 4.8 Å and 4.4 Å. Especially the \(d\)-spacing of 5.6 Å is of interest as to date the largest

![Figure A.1: Selected area diffraction patterns of indents containing Si-XIII in (a) plan-view and (b) cross-sectional geometry. The measured \(d\)-spacings are marked in Ångstroms.](image-url)
$d$-spacing reported for any known phase of silicon has been 4.70 Å for the $\{110\}$ plane of Si-III. From these new $d$-spacings a large hexagonal unit cell with $a = 5.54$ Å and $c = 11.00$ Å may be proposed. The calculated $d$-spacings for such a unit cell are given in Table A.6. Therein, the calculated $d$ matching the measured values indicated in Fig. A.1 are marked as bold. Note that the error associated with measurement of the $d$-spacing is up to ±0.1 Å.

<table>
<thead>
<tr>
<th>[hkl]</th>
<th>d [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>002</td>
<td>5.50</td>
</tr>
<tr>
<td>100</td>
<td>4.80</td>
</tr>
<tr>
<td>101</td>
<td>4.40</td>
</tr>
<tr>
<td>102</td>
<td>3.62</td>
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<td>103</td>
<td>2.91</td>
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<tr>
<td>110</td>
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<tr>
<td>111</td>
<td>2.77</td>
</tr>
<tr>
<td>004</td>
<td>2.75</td>
</tr>
<tr>
<td>112</td>
<td>2.47</td>
</tr>
<tr>
<td>200</td>
<td>2.40</td>
</tr>
<tr>
<td>201</td>
<td>2.34</td>
</tr>
<tr>
<td>202</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Table A.6: List of the $d$-spacings calculated for Si-XIII with the proposed hexagonal unit cell of $a = 5.54$ Å and $c = 11.00$ Å.
Appendix B

Further Details of the TEM Analysis of Pure Amorphous Silicon
In this appendix potential problems with the plan-view sample preparation for TEM are first presented before details of the analysis of the quantitative electron diffraction are given.

**B.1 Crystallization of Pressure-Induced Amorphous Silicon during Plan-View Sample Preparation**

Wet-etching of silicon is usually performed with KOH or with mixtures of HF:HNO$_3$ \[237\]. Etching with KOH however, proved impossible in the case of the PI a-Si as the c-Si matrix etched faster than the a-Si leaving the microindents unconnected to the TEM specimen. Therefore, the wet-etching was performed with mixtures of HF:HNO$_3$:CH$_3$COOH \[238\]. As-indented PI a-Si however, proved especially unstable under these etching conditions as the heat evolution during the etching process could potentially crystallize the a-Si. Therefore, great care had to be taken when measuring the samples by FEM, for example, as sometimes the crystalline layer overlaying the a-Si was very thin.

In one case SAPD analysis of the sample in the TEM dedicated for the FEM showed only amorphous rings. However, when the sample was checked in another TEM, clear evidence of crystallinity could be observed. A dark-field image of this sample together with a bright-field image of the placing of the selected area aperture and the resulting SADP are shown in Fig. B.1(a) through to (c).

This problem proved especially onerous in the electron diffraction experiment. The wet-etch used for the sample preparation was a very fast etch thus reducing the problem of crystallization. However, for the electron diffraction experiment the samples had to be etched in a HF:H$_2$O mixture in order to strip off the native oxide. Although pure HF (or a HF:H$_2$O) mixture is not meant to etch silicon itself, the heat release seemed sufficient to crystallize the sample. This became evident when one PI a-Si sample, which had been checked for its amorphicity in the TEM prior to etching, was observed to be fully crystallized by the etching process. Therefore, great care had to be taken to keep the etch time as short as possible and also to check the area used for the electron diffraction carefully for its amorphicity.

**B.2 Details of the Analysis of the Radial Distribution Functions**

In this section further information about the analysis of the electron diffraction data is presented. First details to the determination of the coordination numbers (CN) will be given. Thereafter, the full particulars for the peak assignment used in Section 7.3.1 in
Further Details of the TEM Analysis

Figure B.1: Example of a sample which had appeared amorphous at first: (a) Original DF image of an area of the as-indented PI a-Si, (b) region the selected area aperture was placed over and (c) the resulting SADP with the crystalline reflections marked with arrows. The images were taken with the CCD camera of the IVEM Hitachi located at Argonne National Laboratory.
Chapter 7 are discussed. Finally, the results from the peak fitting of $G(r)$ are tabulated.

B.2.1 Details of the Determination of the Coordination Numbers

In electron diffraction the CN is usually determined by integration of the first peak of the RDF within some limits on $r$ on either side of the peak. The values presented in Table 7.2 in Chapter 7 however, had been obtained from Gaussian fits to this first peak to avoid inconsistencies in the determination of these limits on $r$. In order to validate this analysis the CNs were also calculated for each measured area using the more traditional integration. Where applicable, the minimum on the side of this first peak was chosen as the integration limit, otherwise the saddle point was used. The integration was performed using the package Origin [137] employing the trapezoidal rule. The averaged CNs for the different forms of a-Si from these Gaussian fits as well as from the integration are summarized in Table B.1 and the uncertainty is the standard error from the different areas measured per form of a-Si. Clearly, the CNs for each form of a-Si are the same within error independent of the mode of determination validating the determination of the CNs by Gaussian fits. Additionally, the average peak widths obtained from the Gaussian fits as well as from the integration are given for each form of a-Si. Although the values are somewhat different depending on the mode of determination, the trends are the same in both cases: the widths of the as-implanted and both relaxed cases are the same, whereas the width of the as-indentated case is clearly increased.

Possible Errors in the Determination of the Coordination Number

As mentioned in Section 7.3.2 in Chapter 7 there are two main systematic errors which could be problematic when determining the CN from an RDF: These are an incorrect mass density $\rho_0$ used to calculate $J(r)$ and/or an incorrect determination of the number of scattering atoms $N$. Such systematic errors were investigated in some depth. Firstly, the influence of $\rho_0$ will be considered and thereafter the influence of $N$.

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>CN from Integr.</th>
<th>CN from Fit</th>
<th>Width from Integr.</th>
<th>Width from Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-imp.</td>
<td>3.81 ± 0.09</td>
<td>3.79 ± 0.11</td>
<td>0.39 ± 0.01</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>rel. imp.</td>
<td>3.78 ± 0.08</td>
<td>3.83 ± 0.08</td>
<td>0.39 ± 0.01</td>
<td>0.34 ± 0.01</td>
</tr>
<tr>
<td>as-ind. PI</td>
<td>3.67 ± 0.20</td>
<td>3.65 ± 0.18</td>
<td>0.54 ± 0.02</td>
<td>0.40 ± 0.02</td>
</tr>
<tr>
<td>rel. PI</td>
<td>3.69 ± 0.11</td>
<td>3.69 ± 0.11</td>
<td>0.39 ± 0.01</td>
<td>0.35 ± 0.03</td>
</tr>
</tbody>
</table>

Table B.1: Average coordination number and average peak width from fitting and integration.
Further Details of the TEM Analysis

It is not clear how much the mass density influences the CN and therefore the possibility of ‘wrong’ mass densities needs to be investigated in more detail. However, the EELS mass densities of 0.049 atoms/Å$^3$ measured in this work for both ion-implanted cases are the same as determined and used by Laaziri et al. [14]. Therefore, only the mass densities of the PI forms of a-Si need to be considered. As discussed in Section 4.3.4, the mass density of PI a-Si might potentially be underestimated by the EELS measurement. Thus this possibility was investigated and a mass density of PI a-Si higher than that of c-Si was assumed: namely 0.051 atoms/Å$^3$, which represented a 2% overestimation of the mass density.

With this assumed mass density the CN was calculated as before. This procedure yielded a CN of $3.68 \pm 0.21$ from the integration and of $3.73 \pm 0.19$ from the Gaussian fit, which is $\sim 0.2\%$ and $\sim 2\%$ higher, respectively, than determined for the actual (measured) mass density. The standard error from the various areas is significantly higher than this deviation ($\sim 5\%$) making the influence of an underestimated mass density less relevant. Note that the peak width is not influenced by uncertainties in the mass density on such a scale and remains $0.54 \pm 0.02$ and $0.40 \pm 0.02$, respectively.

The number of scattering atoms $N$ also has direct influence on the CN determined. As detailed in Section 2.3.2 the reduced intensity function $\phi(k)$ is determined from the intensity $I(k)$ measured from the diffraction pattern using equation 2.16. In practice, this means the intensity $I(k)$ needs to be normalized by ensuring the correct number of scatters is used. This normalization is usually only dependent on two variables, a baseline fit and $N$. If this normalization is performed inaccurately, the resulting $\phi(k)$ will be inaccurate thus yielding inaccurate RDFs. Multiple scattering events, for example, or also low frequency oscillations may prevent the accurate determination of $N$. Note that in this present study the foils were kept thin to reduce such multiple scattering to a minimum.

In order to investigate this influence of $N$ on the CN, a representative area of as-implanted a-Si was investigated with intentionally over- and underestimated $N$. The original $N$ used for this area had been 3630 and therefore $\phi(s)$ with $N$ underestimated as well as overestimated by 200 and 400 atoms was analysed. The parameter $s$ is commonly used in electron diffraction and is correlated to $k$ by $k = 2\pi s$. These ‘wrong’ normalizations of $I(s)$ are shown in Fig. B.2 together with the resulting $\phi(s)$. In all cases the correct normalization of $N = 3630$ (red line) is shown for comparison. The normalizations with the over-/underestimation by 200 atoms are shown in Fig. B.2(a) and the resulting $\phi(s)$ in Fig. B.2(b). Clearly these normalizations are only marginally acceptable with $\phi(s)$ oscillating somewhat around zero, but considerably worse than the normalization with $N = 3630$. Normalizations with an over-/underestimation of 400 atoms are shown in Fig. B.2(c) and the resulting $\phi(s)$ in Fig. B.2(d). These can basically be deemed unacceptable as these $\phi(s)$ do not oscillate around zero.

Nonetheless, from all these $\phi(s)$ the $J(r)$ was calculated in order to evaluate the max-
Appendix B

Figure B.2: Normalization of $I(s)$ with varying $N$. Just acceptable normalizations are shown in (a) with the resulting $\phi(s)$ shown in (b). Clearly unacceptable normalizations are shown in (c) with the resulting $\phi(s)$ shown in (d). The normalization with $N = 3630$ used for the analysis is shown in all figures.

<table>
<thead>
<tr>
<th>$N$</th>
<th>CN from Integr.</th>
<th>CN from Fit</th>
<th>Width from Integr.</th>
<th>Width from Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>3230</td>
<td>3.87</td>
<td>3.85</td>
<td>0.37</td>
<td>0.310</td>
</tr>
<tr>
<td>3430</td>
<td>3.82</td>
<td>3.80</td>
<td>0.38</td>
<td>0.317</td>
</tr>
<tr>
<td>3630</td>
<td>3.77</td>
<td>3.77</td>
<td>0.38</td>
<td>0.325</td>
</tr>
<tr>
<td>3830</td>
<td>3.73</td>
<td>3.73</td>
<td>0.40</td>
<td>0.328</td>
</tr>
<tr>
<td>4030</td>
<td>3.69</td>
<td>3.69</td>
<td>0.40</td>
<td>0.329</td>
</tr>
</tbody>
</table>

Table B.2: Coordination number and width of first peak of the $J(r)$ from integration and fitting with a Gaussian depending on the number of scatterers $N$.

The range of ‘acceptable’ normalization results in an over-/underestimation of the CN by $\sim 1\%$. Even significant over-/underestimation of $N$ results only in a deviation of $\sim 3\%$. Note that the standard error resulting from averaging over a number of areas used per form of a-Si had also been $\sim 3\%$. It seems highly unlikely that for all areas measured
Further Details of the TEM Analysis

for one form of a-Si, $N$ would be consistently over- or underestimated. Rather a mix of overestimated and underestimated $N$ would be expected for the five areas used per form of a-Si. Therefore, this systematic error is also not expected to influence the determination of CN significantly making the obtained results relevant.

B.2.2 Peak Assignment

As detailed in Fig. 7.2(b) in Section 7.3.1 the reduced RDFs were divided into three regions A, B and C. Whereas region A consists clearly of one peak, the first nearest-neighbour, the situation is more complex for regions B and C. In previous work only one peak was fitted to region B, since, for example, the asymmetry was less apparent in previous electron diffraction studies on a-Si:H [140] or X-ray diffraction studies on thick ion-implanted films [14]. In the latter case however, an asymmetry of the second peak was noted and attributed to a possible third peak. In the present study this peak in region B is clearly asymmetric and could not be fitted with one Gaussian, but only with two. An example of such a fit with two Gaussians is shown in Fig. B.3.

For c-Si the peak assignment is clear, with the first peak at 3.84 Å within region B corresponding to the second-nearest neighbours, the 12 two-bond atoms. The third-nearest neighbour (or second peak in region B) at 4.5 Å corresponds to one of the two different ‘types’ of three-bond atoms [239]. No clear peak is visible at this distance in the reduced RDF of any form of a-Si although other studies have reported small peaks at 4.5 Å after annealing [12, 14, 221]. The absence of a distinct peak at 4.5 Å has been attributed to the ability of adjacent tetrahedra to rotate about the common bond (see for example Ref. [24] and references therein).

However, all these above studies on a-Si investigated the $J(r)$ [or $T(r) = g(r) = J(r)/r$] rather than $G(r)$.

![Figure B.3: Example of a fit with two Gaussians to the second peak of a reduced RDF obtained from as-implanted a-Si.](image)
made fitting of the high-$r$ regime of region B impossible or at least difficult. In fact, most studies only fitted the low-$r$ side of the peak in region B. Hence, the asymmetry of the peak in this region has not previously been noted or at least not been investigated in detail. As this second peak within region B is clearly present in this work here, it has to be assigned to the same three-bond atoms as those resulting in the peak at 4.5 Å for c-Si.

Similar to region B, region C can also be decomposed into two peaks. In the case of c-Si, the fourth-nearest neighbour at 5.43 Å can be attributed to the closest four-bond atoms [239]. The intensity of this peak is lower as only 6 four-bond atoms can be found at this distance. The fifth-nearest neighbour at 5.92 Å however, also originates from 12 three-bond neighbours and thus has a higher intensity. This seems to be reflected in the reduced RDFs of a-Si, with the peak in region C being clearly asymmetric, whereby the peak on the high-$r$ side seems to be larger than the peak on the low-$r$ side. Therefore, region C is also fitted with two Gaussians rather than one and the two peaks are assigned as the fourth- and fifth-nearest neighbours.

As noted in Section 7.3.1 an additional small peak can be observed at $\sim$2.85 Å whose origin remains unclear. One possibility could be contamination through impurities introduced during the sample preparation process. However, none of the major suspects fits this peak. For example, the hydrogen present within the network of a-Si:H is not very well represented in the RDF making it an unlikely candidate [42]. Carbon contamination seems also unlikely as an RDF of SiC would have peaks at 1.55 Å, 2.58 Å, 1.93 Å and 2.91 Å with the first two peaks being the first two C-C peaks and the latter two the first two Si-C peaks [240]. Lastly, fluorine remaining from the etching process would be most likely trapped as silicon tetrafluoride molecules within the network [241]. The Si-F bond-length in this molecule is 1.54 Å, but no peak can be observed at this position making its presence also unlikely.

Although the native oxide has been stripped off with a HF:H$_2$O etch directly prior to TEM examination, oxide seems to be the most likely candidate for contamination and is thus considered in more detail. Amorphous SiO$_x$ is a tetrahedrally bonded system wherein the Si-O bond length is $\sim$1.62 Å and the Si-Si bond-length the same as in a-Si/c-Si at $\sim$2.35 Å. The next peaks in the RDF resulting from an O-Si-O bonding and an O-Si-Si bonding are observed at 2.65 Å and 3.07 Å, respectively. The next pure Si-Si neighbouring (a Si-O-Si bonding) is expected at 3.12 Å. Experimentally, the peaks from the O-Si-Si bonding and the Si-O-Si bonding merge into one peak at $\sim$3.11 Å (for further details, see Refs. [242] and [243] and references therein). Since the RDFs presented here possess local minima at $\sim$1.65 Å, $\sim$2.7 Å and $\sim$3.0 Å, it seems very unlikely that this peak at 2.85 Å can be attributed to the presence of oxygen. However, this result may suggest that the stripping of the native oxide by wet-etching was successful.

Another possibility is that the peak at $\sim$2.85 Å may inadvertently be correlated to the removal of the native oxide which had taken place prior to the TEM experiment. Previ-
Further Details of the TEM Analysis

ously a study on vitreous silica by reflective high-energy electron diffraction employed to characterize the top 1-2 nm of the material and X-ray diffraction employed to characterize the bulk observed interesting differences [244]. A distinct peak at 2.9 Å was observed solely for the surface RDF and this was attributed to a decrease in the Si-Si interatomic spacing at the surface, i.e. to a reduction in the bond-angle of the Si-O-Si bonding. It may be possible that in this present case, some Si atoms remain in this strained surface configuration although the O atoms or near-surface SiO\text{x} configuration have been removed by the etching. Therefore, this small peak may be tentatively assigned to effects resulting from the high surface-volume ratio of such very thin foils and resulting prominence of strained bonds on the surface.

B.2.3 Results from the Peak Fitting

All peaks of \( G(r) \) were fitted with Gaussians using the package Origin [137]. The fit was of the form:

\[
y = y_0 + \frac{A}{w\sqrt{\pi/2}} e^{-\frac{2(x-x_c)^2}{w^2}}
\]

with the fit parameters \( y_0 \) (the baseline), \( x_c \) (the peak position), \( A \) (the peak area) and \( w \) (the peak width).

The results from these fits are summarized for all forms of a-Si for the peak positions in Table B.3, for the peak areas in Table B.4 and for the peak widths in Table B.5. The values are the averages from the different areas measured per form of a-Si and the uncertainty is the standard error. The same fits were performed for the simulated c-Si structure and the obtained values are shown for comparison. From these results the peak height \( h \) of the Gaussians was calculated by \( h = A/(w\sqrt{\pi/2}) \) for each individual area. The peak heights for the different forms of a-Si are summarized in Table B.6 and the values are again the averages with the uncertainty being the standard error. Note that this peak height is the total height of the respective peak and not the height starting from zero indicating that these calculated peak heights are in good agreement with the peak heights visually measurable in Fig. 7.2. The ratio of these peak heights calculated for each measured area to the respective peak width was determined. These ratios are again averaged for each peak and form of a-Si and are summarized together with the standard error in Table B.7. The ratio of peak area 4 to peak area 1 as well as the ratio of peak area 4 to region B (i.e. the sum of peak areas 2 and 3) was also calculated for each individual measured area. The averaged ratios are shown together with the standard error in Table B.8.