Structural Characterization of Amorphous Silicon

Bianca Haberl

A thesis submitted for the degree of Doctor of Philosophy of The Australian National University

December 2010
Chapter 3

Forms of Amorphous Silicon
Amorphous solids can be formed by a multitude of different methods. However, all these methods can be classed into three basic types: by condensation of vapours onto a substrate, by rapid quenching from the melt and by solid-state amorphization. The first method includes both chemical and physical vapour deposition techniques. In the former case the vapour is created through a chemical reaction in a gas and in the latter case from a solid. Such condensation of amorphous solids was achieved as early as 1954 for amorphous metals at low temperatures [160, 161]. The next principle method for the formation of amorphous solids is by quenching from the liquid form. This is used extensively for polymers, ceramics and metallic systems [162] and was first used and described in 1960 for gold-silicon alloys [163]. In the 1960s further methods were implemented for the formation of amorphous solids which allowed for amorphization directly from the solid-state. This solid-state amorphization includes a variety of techniques such as hydrogen absorption for metal alloys, ball milling, irradiation [164] and pressure-induced amorphization (see for example Ref. [165] and references therein).

Very different properties are expected to result from such varied formation processing of amorphous solids and in particular for a-Si. Therefore, in this study a-Si prepared by all three principle methods was investigated. Firstly, a-Si made by chemical and physical vapour deposition was prepared by plasma-enhanced chemical vapour deposition and magnetron-sputtering, respectively. Additionally, a-Si was quenched from a laser-induced melt, the so-called laser-quenched a-Si. Lastly, a-Si was prepared by self-ion implantation (i.e. irradiation) and by fast indentation unloading (i.e. pressure-induced). Furthermore, the influence of ex situ thermal annealing on all forms of a-Si was investigated since the annealing behaviour is only well understood for the case of ion-implanted a-Si.

These five very different forms of a-Si prepared for this work will be introduced in this chapter. Additionally, the experimental conditions under which the different forms of a-Si were prepared and thermally annealed are detailed.

### 3.1 Hydrogenated Amorphous Silicon

Whereas pure a-Si is often cited as a model system of an amorphous semiconductor, hydrogenated amorphous silicon (a-Si:H) has many technological applications including photovoltaic cells [9] or thin-film transistors [8]. Furthermore, as a-Si:H can be easily doped [166] it is suitable for a range of devices. Due to the high hydrogen content however, its structure cannot be described as a CRN or even a defective CRN. Most commonly therefore, its structure is described by the hydrogen glass model [167]. In this model a-Si:H is treated as a $Si_{1-x}H_x$ alloy with usually $x \geq 0.1$ to account for the importance of hydrogen. This alloy consists of an a-Si matrix with a glasslike hydrogen submatrix [167] and hence the structural properties of a-Si:H differ substantially from pure a-Si. Therefore, this study will not focus on the structure of a-Si:H in depth as completely different
mechanisms are involved in this case. Nonetheless, the deformation behaviour under indentation testing is of some interest as questions remain regarding the influence of H on the probability of phase transformation under indentation testing.

Such a-Si:H films are most commonly prepared by plasma-enhanced chemical vapour deposition (PECVD) from silane, SiH$_4$. Thereby silane is either pure or mixed with hydrogen and/or argon and the silane molecules are dissociated by the use of a plasma [167, 168]. The plasma is usually induced by a radio-frequency (RF) power supply applied to two electrodes. The substrate onto which the layer is to be deposited is placed on top of one of the electrodes within a vacuum chamber [168]. This process is shown schematically in Fig. 3.1

Early on, it was recognized by Knights et al. that sub-optimal deposition conditions can lead to unwanted morphology such as columnar growth, whereby the regions adjoining the columns are voids [169]. Thus the structure of the resulting film depends strongly on a variety of parameters, such as the plasma, the gas, the gas flow rate, the RF power and the substrate temperature. Therefore, great care has to be taken when selecting the deposition conditions in order to tailor the film for the subsequent use [167].

The samples studied here were deposited at the Semiconductors & Solar Cells Group at the College of Engineering & Computer Science of the Australian National University. Several samples were deposited for various length of time in a Roth & Rau AK400 PECVD system. The growth conditions for the respective deposition time are summarized
Chapter 3: Forms of Amorphous Silicon

<table>
<thead>
<tr>
<th></th>
<th>6 min</th>
<th>18 min</th>
<th>30 min</th>
<th>30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma power</td>
<td>650 W</td>
<td>650 W</td>
<td>650 W</td>
<td>650 W</td>
</tr>
<tr>
<td>RF bias voltage</td>
<td>150 V</td>
<td>150 V</td>
<td>150 V</td>
<td>150 V</td>
</tr>
<tr>
<td>SiH$_4$ flow</td>
<td>30 sccm</td>
<td>30 sccm</td>
<td>30 sccm</td>
<td>8 sccm</td>
</tr>
<tr>
<td>Ar flow</td>
<td>30 sccm</td>
<td>30 sccm</td>
<td>30 sccm</td>
<td>8 sccm</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>0.15 mbar</td>
<td>0.15 mbar</td>
<td>0.15 mbar</td>
<td>0.2 mbar</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>200°C</td>
<td>200°C</td>
<td>200°C</td>
<td>300°C</td>
</tr>
</tbody>
</table>

Table 3.1: Summary of RF power, flow rates in standard cubic centimeters per minute (sccm), pressure and substrate temperature used for the different growth conditions in the PECVD chamber.

In Table 3.1. In all cases the substrate was a single crystal Cz Si(100) wafer, p-doped with boron to a resistivity of 10-20 Ωcm.

However, device-quality a-Si:H films can also be created by other means such as hot-wire chemical vapour deposition (HWCVD) [170] or reactive magnetron-sputtering [171, 172]. Moreover, both these techniques allow formation of a-Si films with a significantly lower H content and increased mass density [173, 174]. The latter of these two techniques will be introduced in the next section.

### 3.2 Magnetron-Sputtering

Sputter-deposition is a physical vapour deposition method based on ejecting (i.e. ‘sputtering’) atoms from a target by bombardment with energetic ions [168, 175, 176]. Therefore, a plasma which supplies the ions (usually of a noble gas like argon) is created between two electrodes in each source, known as a gun. Thereby, the target material acts as an electrode. RF rather than DC diode sputtering is widely used, since this enables insulating targets to be sputtered. The ions will bombard the target in order to set off collision cascades resulting in recoil atoms in the target. When such a recoil atom reaches the surface with sufficient energy it will be ejected from the target into the gas phase. If the pressure in the chamber is sufficiently low the atoms will condense on a substrate placed in the chamber.

The sputter yield can be increased by the use of magnetron-sputtering whereby a magnet is placed behind the cathode. This magnetic field in addition to the electric field from the electrodes will constrain secondary electron motion to the vicinity of the target resulting in more collisions per electron and thus increasing the sputter rate [175]. Additionally, these electrons are not free to bombard the substrate and this is expected to increase the
Section 3.2: Magnetron-Sputtering

Figure 3.2: Schematic of the deposition process in a magnetron-sputter chamber.

a-Si film quality [176]. Furthermore, the increased ionization efficiency allows the discharge to be maintained at lower operating pressure [175] also potentially increasing the film quality. Such a chamber is shown schematically in Fig. 3.2.

It has been shown that the geometry of the sputter apparatus will influence the resulting morphology and topology of the coating significantly [177]. To account for these effects, structure-zone models have been developed depicting the influence of the sputter variables [168, 177]. This zone structure can result in reduced mass density when compared to the bulk density as a result of porosity. The porosity can be exhibited in macro-, micro- as well as nanocolumns and is most commonly due to the inclusion of Ar into the film [168].

In order to deposit pure a-Si, a pure silicon target is used for the sputtering. However, if one wants to grow a-Si:H rather than a-Si by sputter-deposition, hydrogen gas is added to the argon sputtering gas [171, 172]. With the addition of this gas, formation of silicon hydrides can occur at the target surface. This leads to ejection of surface species through chemical sputtering effects. These species as well as neutral hydrogen atoms from the plasma condense on the substrate and form a-Si:H. This process is called reactive magnetron-sputtering which is used to deposit device-quality films [171]. Interestingly, films grown by reactive magnetron-sputtering containing a relatively low atomic percentage of H did appear featureless in a cross-sectional scanning electron microscope study [171]. Only the films with a high H content displayed a ‘rippled’ morphology which
was different to the columnar morphology observed in PECVD films.

The structural properties of such sputtered a-Si:H and a-Si have been studied in great detail. For example, Raman microspectroscopy on reactive RF-sputtered a-Si showed a distinct correlation between structural order and substrate temperature during deposition [135]. The order as expressed by the bond-angle distortion was found to increase with increasing substrate temperature up to \( \sim 300^\circ C \), whereafter it decreased again. No such peak was observed for RF diode sputtered a-Si (RF sputtering without the magnets) where the short-range order was observed to continually increase for all substrate temperatures tested (the maximum temperature was well above 500°C). Moreover, in the first study a significant order gradient was observed along the growth axis with the top surface being less ordered than the deep region [135]. This was later attributed to different hydrogen content in the surface and the deep region [136] as hydrogen is well known to improve the structural order of sputtered a-Si as measured by Raman microspectroscopy [178]. Interestingly, most previous fluctuation electron microscopy studies of a-Si have also been performed on magnetron-sputtered a-Si [15, 50, 51, 146, 148, 153] thus providing useful additional insights into the structural properties of this form of a-Si.

Magnetron-sputtered a-Si was chosen as the main form of deposited a-Si studied in this thesis. It may be possible to lower the H content further by the use of films deposited by HWCVD [174], but no previous FEM work has been performed on these films. As one of the major points of this work is to investigate the influence of thermal annealing on the structure, comparison to previous work is an advantage.

The magnetron-sputtered material was deposited with an AJA ATC 2400-V UHV system located at the Australian National University using a 3-inch Si target of 99.999% purity. Two sputter-depositions at different substrate temperatures were performed, one at room temperature and one at a nominal temperature of 300°C. The final film thickness in both cases was \( \sim 500 \) nm. In both cases the substrate onto which the film was deposited was a single crystal Cz Si(100) wafer, p-doped with boron to a resistivity of 10-20 \( \Omega cm \).

The exact sputter conditions are summarized in Table 3.2.

### Table 3.2: Summary of the sputter-deposition conditions used in this thesis.

<table>
<thead>
<tr>
<th></th>
<th>RT</th>
<th>300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>238 W</td>
<td>298 W</td>
</tr>
<tr>
<td>RF bias voltage</td>
<td>120 V</td>
<td>130 V</td>
</tr>
<tr>
<td>Ar flow</td>
<td>19.8 sccm</td>
<td>19.8 sccm</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>3.7 mT</td>
<td>3.7 mT</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>( \sim 2.3 ) nm/min</td>
<td>( \sim 2.7 ) nm/min</td>
</tr>
</tbody>
</table>
Even in the best ultra-high-vacuum systems, deposited films always contain a small number of impurities such as hydrogen or oxygen. The other forms of a-Si studied in this work are prepared from bulk c-Si and are thus expected to be as pure as the starting c-Si itself. These forms will be introduced in the next sections.

### 3.3 Laser-Induced Melting and Quenching

In 1979 Liu *et al.* observed the formation of an amorphized zone after melting of single crystal silicon by a single picosecond laser pulse [179]. Depending on the intensity either amorphous ring patterns or, for lower intensities, amorphous spots were reported. The amorphicity of these zones was confirmed by electron diffraction experiments. It was concluded that a-Si only forms when the melt is undercooled to beneath the melting temperature of a-Si (which is lower than the melting temperature of c-Si). This then allows the direct nucleation of a-Si. If the temperature of the molten layer remains well above the melting temperature of c-Si instead, longer cooling rates are expected which will result in the nucleation of c-Si. Additionally, a cross-sectional TEM study confirmed that a-Si layers formed by laser melting are indeed uniform and indistinguishable from other forms of a-Si using standard techniques [180].

With the advent of femtosecond lasers, the influence of even shorter laser pulses on the formation of a-Si zones was investigated [181]. Several different morphological features are observed for such short pulses, namely: oxidation, amorphization, re-crystallization, the formation of bubbles due to boiling below the surface and ablation. Furthermore, features such as ripple formation, columnar growth and crater formation due to material removal occur after exposure to multiple pulses. Thus, although the process of amorphiza-

![Figure 3.3: Schematic of the formation of laser-quenched a-Si through fast femtosecond laser melting.](image-url)
Chapter 3: Forms of Amorphous Silicon

tion and crystallization from the melt is similar to picosecond laser pulses other undesir-
able features are present. For example, due to layer boiling, inhomogeneous nucleation
of bubbles is observed in regions of higher laser fluences and thus regions of higher tem-
perature and slower cooling rates [182]. Nonetheless, the possibility of the formation of
a-Si in the laser-modified zones has been confirmed by Raman microspectroscopy [183]
as well as cross-sectional TEM [184].

However, little is known about the structure of the amorphous silicon created by rapid
quenching from the melt. Therefore, in the present study laser-quenched a-Si was formed
by multiple shots of femtosecond pulses onto single crystal silicon. This resulted in some
cases in a crater with a further modified zone surrounding the crater and in other cases in
modified zones without a crater. Such a formation of a crater surrounded by an amorphous
zone is shown schematically in Fig. 3.3. The samples were prepared at the Université de
Montréal with a Hurricane, Spectra Physics Ti:sapphire laser.

3.4 Ion-Implantation

Ion implantation has proven to be a very useful technique for the controlled modification
of a large number of solids [164] and especially for semiconductors [164, 185]. Addition-
ally, full solid-state amorphization can be induced by a sufficiently high irradiation dose.
Such full amorphization was first observed on uranium-iron alloys after neutron irradia-
tion [186]. The amorphization of silicon by ion-implantation has attracted wide interest
over the last decades since this a-Si is a model system for study, including its crystalliza-
tion properties [59], and in addition such amorphization is central to dopant introduction
in device fabrication [187]. Creation of a-Si by irradiation is a non-equilibrium process,
which occurs when the free energy of the damaged crystal is higher than of the amorphous
phase [164, 188]. For silicon, this crystalline-amorphous transition can be understood as
the critical balance between damage generation and dynamic annealing and depends crit-
ically on such parameters as implantation temperature [189, 190], ion species [191], dose
[192] and dose rate (see for example Ref [188] and references therein). To produce good
quality amorphous layers free of crystalline regions, dynamic annealing is suppressed by
using a low temperature implantation condition typically at liquid nitrogen temperatures
[190].

In principle, ballistic collisions are responsible for almost all disorder and structural
changes induced in Si by irradiation. Damage results when ions with an energy above
the displacement energy (15 - 20 eV for silicon) impart sufficient energy to a matrix atom
to create a Frenkel (vacancy-interstitial) pair. When the energy of the impinging ion is
sufficiently high, the displaced atom, or recoil, can produce further displacements. Thus,
a collision cascade of displacements can result from collisions of a single ion. Such a
collision cascade is illustrated in Fig. 3.4. Its lifetime is in the order of $10^{-11}$ s and its size
Section 3.4: Ion-Implantation

for Si ion-implantation can be of the order of $10^{-21}$ cm$^3$. Indeed, amorphization of c-Si by Si ion implantation at liquid nitrogen temperature has been observed to result in discrete damaged regions along the entire ion path with the damage density increased close to the end of range [193]. However, it is not only important to understand the defect production by single ions, but even more so the damage accumulation as the fluence increases.

Two main models for the amorphization of silicon have been proposed. In the first model, so-called homogeneous amorphization, a-Si nucleates as a result of a sufficient number of defects produced within collision cascades which are distributed homogeneously throughout the irradiated region. Thus, phase transition is induced by an accumulation of a critical defect concentration in c-Si (for example see Ref. [194]). In the second model, so-called heterogeneous amorphization, amorphous zones created locally within collision cascades by the incident ions accumulate with increasing fluence until eventually they overlap to yield a uniform a-Si layer. Such formation of significant amorphous pockets has been observed in molecular-dynamics (MD) simulations of collision cascades where local heating can lead to localized melting on a very short time scale (a so-called thermal spike) [195]. The rapid quenching of such ‘spikes’ can lead to amorphous zones.

In defect-accumulation models it is essential to identify the defects which can act as amorphous embryos. Vacancies, divacancies, vacancy clusters, self-interstitial clusters and di-interstitial pairs have been proposed. For an extensive review on these defects see Ref. [188]. More recently, Tang et al. identified a new type of defect, the so-called IV pair by MD simulations [196]. The defect was observed when a vacancy approaches a $\langle 110 \rangle$ dumbbell interstitial, whereby a metastable defect structure is generated instead of immediate interstitial-vacancy recombination. This defect consists of a local rearrangement of bonds in the crystal with no excess or deficit of atoms and is hence known as bond-defect. Nonetheless, it introduces the five- and seven-membered rings well known
to exist in a-Si. Based on this defect Pelaz et al. proposed an atomistic model for amorphization which is able to explain and reproduce experimental observations [188]. In this model amorphous layers are particular cases of amorphous pockets which are considered as agglomerates of $IV$ pairs. Whereas a single $IV$ pair has a very short lifetime, a second $IV$ pair will increase this lifetime. Therefore, once a concentration of $\sim 25\%$ is reached, the lattice will spontaneously collapse to a-Si (homogeneous amorphization). Heavier ions however, can induce local amorphous pockets with longer lifetimes which can act as nuclei (heterogenous amorphization). Thus, this model was able to unify these two models conclusively. Additionally, further defects within the network are possible such as, for example, a Si self-interstitial from the incident ion. The model was further extended by Mok et al. to include not just $IV$ pairs, but also $I_2V_2$ as well as $I_nV_m$ pairs [197].

In this study all ion-implantation was performed at liquid nitrogen temperature in order to minimize dynamic annealing. Furthermore, the implantation was performed at a $7^\circ$ tilt to the normal of the wafer in order to avoid channelling effects. All implantation was performed at sufficiently high doses to ensure full amorphization. Moreover, a surface implant was performed in order to ensure a uniform ion-implanted layer. For example, MD simulations of the thickness of an amorphous layer created by 300 keV Si ions observed at a fluence of $1 \times 10^{15}$ cm$^{-2}$ only a buried layer. At a fluence of $5 \times 10^{15}$ cm$^{-2}$ this layer was then found to reach the surface. However, care has to be taken with the experimental set-up as, for example, even implantation at 100 keV with a fluence of $1 \times 10^{15}$ cm$^{-2}$ can yield crystallites on the surface if the implantation current is too high and/or the wafer is not sufficiently cooled [194]. Therefore, to avoid such issues it is best to perform an additional surface implant at energies below 100 keV.

Such implantation conditions are well known to result in a uniform, voidless layer [58] with a density-deficit of less than 2\% when compared to c-Si [23].

All implantation was performed at the ANU 1.7 MV NEC tandem high energy ion-implanter and the ANU 175 kV low energy ion-implanter. In general, an ion-implanter consists of an ion-source to produce an ion-beam, an ion-accelerator to accelerate the ions to the desired energy for implantation, a high-resolution magnet to select ions of the desired species and a target chamber to house the sample [164, 185]. The beam is scanned across the wafer until the required implant dose is achieved. The implantation is carried out under vacuum, whereby the sample is thermally bonded in order to ensure an implantation at liquid nitrogen temperature. The implantation conditions used in this study are summarized in Table 3.3.

Multiple ‘thick’ samples were prepared by implantation of single crystal Cz Si(100), p-doped with boron to a resistivity of 10-20 $\Omega$cm. The implantation conditions used resulted in a continuous surface layer of $\sim 2 \mu$m. These samples were used for all indentation, Raman microspectroscopy, FEM and EELS studies. The ‘thin’ sample was prepared by implantation into a 7 $\mu$m epilayer of Si(100), p-doped with boron to a resistivity of
3.5 Pressure-Induced Phase Transition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy [keV]</th>
<th>Fluence [cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘thick’</td>
<td>80</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td>‘thin’</td>
<td>50</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>$5 \times 10^{15}$</td>
</tr>
</tbody>
</table>

Table 3.3: Summary of the fluence and energies used for the ion-implantation. Both sets of ion-implantation were performed at liquid-nitrogen temperature at a 7° tilt to the normal of the wafer.

10-20 $\Omega cm$ on a c-Si substrate. The implantation conditions used in this case resulted in a continuous surface layer of $\sim$300 nm. This sample was used for the electron diffraction study. Both sets of samples, ‘thick’ and ‘thin’, were probed for their film thickness using Rutherford backscattering spectrometry. Note that the different implantation conditions for the various TEM plan-view samples do not have any significant influence since in such a sample only the top surface, i.e. the region affected by the lowest implant energy, is studied.

3.5 Pressure-Induced Phase Transition

Pressure-induced (PI) amorphization has been observed for many solids such as elements, compounds and alloys. The first PI amorphization was observed as early as 1965 on the system Ga-Sb (Refs. [198] and [165] and references therein). In this early study, Ga-Sb was pressurized in order to induce a phase transformation to a metallic GaSb-II and then cooled to liquid-nitrogen temperature. Upon pressure release at this low temperature and subsequent heating to room temperature the material transformed to an amorphous phase. Further PI amorphization was thereafter observed for Gd$_2$(MoO$_4$)$_3$ in 1972 [199] and Zn-Sb alloys in 1975 [165]. However, in all these studies the amorphous forms were only of secondary interest and therefore not investigated in detail [165].

The first material where the PI amorphization was investigated in detail was water ice [200, 201], In these studies, crystalline ice was pressurized at 77 K to 1.5 GPa resulting in the formation of high-density amorphous ice. Since then a great number of solids have been observed to undergo PI amorphization, compounds such as SiO$_2$ or SnI$_4$, as well as alloys such as Cd-Sb or Zn-Sb (for details refer to Ref [165] and references therein).
Interestingly, MD simulations showed specific thermodynamic parallels between such solid-state amorphization and melting [202]. Although this study explicitly excluded materials which densify upon melting such as silicon or ice, such a relationship was later shown to also apply to ice [203].

Matters are more complex in the case of silicon however, as no direct solid-state amorphization without an intermediate state has been observed. Nonetheless, in 1988 Clarke et al. observed in a TEM study that, upon indentation loading and unloading, PI amorphization occurs in c-Si as well as crystalline germanium [89]. Additionally, in situ electrical measurements confirmed the formation of a metallic phase under indentation loading cycle which was assumed to be Si-II. Therefore, the formation of a-Si was attributed to the fast unloading rate (with a rate of 16.67 N/s) from this metallic phase that prevented the nucleation of the high-pressure crystalline end phases that normally occur. Moreover, a diamond-anvil cell study on c-Si reported the formation of a-Si if pressure release occurred at temperatures below 120 K [86]. Furthermore, an indentation study of c-Si as well as a-Si observed the formation of PI a-Si upon indentation unloading at 77 K although the formation of the crystalline high-pressure phases had been observed in both cases under the same conditions at room temperature [204]. However, to the best of my knowledge, no DAC studies have observed the formation of a-Si from bulk c-Si if loading as well as unloading was performed at room temperature.

Despite PI amorphization of c-Si being difficult to achieve in DACs, it has proven very easily achieved by indentation. Note that the formation of PI a-Si by indentation is the same as the pressure-induced amorphization in DACs. PI a-Si results from the hydrostatic component of the indentation stress, i.e. the phase transition, and not from the shear stress component. This formation from Si-II by rapid indentation unloading is shown schematically in Fig. 3.5. For example, rapid unloading when using a Berkovich tip results in an ‘elbow’ event in the load-displacement curve and reliably produces PI a-Si [95, 120]. Additionally, TEM analysis of residual indents from spherical indentation employing the load-partial-unloading cycle mentioned in Section 2.1.1 in the previous chapter observed the formation of such PI a-Si [97, 98]. However, formation of PI a-Si after fast unloading from spherical indentation appeared less reliable, with the ‘elbow’ event being more subtle than after Berkovich indentation [121]. Therefore, residual indents nominally consisting of PI a-Si have to be checked with Raman microspectroscopy for the presence of crystalline high-pressure phases.

Despite the ease of the formation of PI a-Si very little is known to date about its structure. Only one study on the structure of PI a-Si has been performed by electron diffraction [205]. This study reported structural differences between PI a-Si formed directly by rapid unloading and by slow unloading in conjunction with the formation of the high-pressure phases. These structural differences were attributed to differences in nearest-neighbour distances arising from slightly different formation methods. However, the interpretation
from this study is somewhat inconsistent with the LDA and HDA silicon reported from DAC experiments. Therefore, the structural properties of PI a-Si need to be better understood.

The PI a-Si used in this study was formed using the UMIS with a spherical diamond indenter of \( \sim 18 \mu m \) radius at room temperature and ambient pressure. Large arrays of indentations were performed on single crystal Cz Si(100), p-doped with boron to a resistivity of 10-20 \( \Omega \text{cm} \). Two slightly different sets of PI a-Si were formed, one used for structural characterization and one used for a re-indentation study designed to investigate the mechanical properties of PI a-Si.

For the re-indentation study loads of up to 700 mN were applied at an average loading rate of \( \sim 5 \text{ mN/s} \) and unloading was performed within 1 s. This resulted in a transformed zone of PI a-Si of \( \sim 9 \mu m \) diameter and extending \( \sim 400 \text{ nm} \) below the surface. The loading conditions used ensured that no cracking occurred and that the formation of a-Si was much more likely on unloading than the formation of Si-XII/Si-III. Raman microspectroscopy was used to confirm that no crystallites were present within each residual indent, at least to the extent of the sensitivity of the Raman technique.

For the structural TEM studies, loads of up to 750 mN were applied at a loading rate of 5 mN/s, and a fast unloading rate was employed with unloading occurring within 1 s. In this case, cracking was observed occasionally around the residual indent impressions.

### 3.6 Thermal Annealing

For the case of ion-implanted a-Si, thermal annealing at 450\(^\circ\)C for 30 minutes is known to structurally relax the amorphous layer [20]. The different ‘state’ of the ion-implanted a-Si after such a thermal anneal is, for example, represented in the mechanical properties with the annealed form displaying a considerably higher indentation hardness [20].
Furthermore, annealing under these conditions is known to result in epitaxial regrowth of only $\sim 1$ nm [59] which mainly serves to sharpen the a-Si/c-Si interface.

However, little is known about the influence of such \textit{ex situ} thermal annealing on the other forms of a-Si studied in this work. Therefore, all forms of a-Si were annealed under these same conditions in order to allow comparison. This thermal anneal will be referred to as a ‘relaxation anneal’ throughout the remainder of this work.

Such a relaxation anneal was performed on half of each of the samples. The thermal annealing was conducted in a quartz tube furnace at 450$^\circ$C for 30 min in a nitrogen atmosphere. The samples were placed into a quartz-boat and mechanically pushed into the centre of the furnace using a quartz-rod. The push-in and pull-out times were 1 min in all cases.

In addition, some of the magnetron-sputtered a-Si samples where subjected to a further anneal, the so-called ‘argon anneal’. This was performed at 600$^\circ$C for 1 min in a tube furnace in a nitrogen atmosphere with the same push-in and pull-put times of 1 min. This ‘argon anneal’ was performed in order to drive out the argon introduced during the sputtering process and thus change the structural properties.
Chapter 4

Initial Characterization of the Amorphous Films
4.1 Introduction

As detailed in the previous chapter, the various forms of a-Si studied in this work are created by very different means: by chemical vapour deposition, by physical vapour deposition, by quenching from the melt, by ion-implantation and by rapid depressurization of a metallic phase. Therefore, significant differences in their bulk characteristics, such as, for example, in their impurity content, mass density or even residual crystallinity are to be expected. Additionally, some of these films might exhibit small-scale density fluctuations such as nanopores or voids.

These properties can significantly influence the investigation by the techniques detailed in Chapter 2. For example, too large density fluctuations of the film can prevent the investigation by FEM as uniform areas are required for this technique. Another example is crystallinity, which can prohibit the analysis of the amorphous network by Raman microspectroscopy, since the influence of nanocrystals on the spectrum might not be distinguishable from the order of the amorphous network. Therefore, it is essential to investigate these properties prior to the detailed characterization of the structural properties. Based on the findings from this investigation it can then be decided which forms of a-Si can be studied in more depth. Note that ion-implanted a-Si was not investigated for any of the properties mentioned above, as it is well known to be a pure uniform and voidless [58] form of a-Si. Furthermore, its density-deficit when compared to c-Si is less than 2% [23] making it one of the most dense forms of a-Si studied to date at ambient temperature and pressure.

Firstly, all forms of a-Si were probed for basic film characteristics such as evidence of voids, nanopores or crystallinity by cross-sectional TEM (XTEM). The cross-sections were studied using bright-field imaging, selected area diffraction and dark-field imaging. Raman microspectroscopy was also used to investigate possible traces of crystallinity.

The impurity content of the deposited films was then studied using secondary ion mass spectrometry (SIMS) and Rutherford backscattering spectrometry (RBS). SIMS was employed to investigate the hydrogen and oxygen content of both types of deposited films, prepared by PECVD and magnetron-sputtering. Additionally, the argon content of the sputtered films was determined using RBS. Furthermore, the surface roughness of the magnetron-sputtered films was measured using an atomic force microscope (AFM).

Lastly, the mass density of some of the films was determined since, for example, reduced mass density can indicate porosity of the film [206]. Indeed, this property can indicate the presence of nanopores even if they are not visible by conventional TEM. In the case of the magnetron-sputtered a-Si, RBS was used for this measurement, whereas electron-energy-loss spectroscopy (EELS), as detailed in Section 2.3.4, was employed in the case of PI a-Si. As the measurement of the mass density by EELS is not a standard technique for a-Si and absolute density measurement is not possible without calibration,
the mass density of ion-implanted a-Si was measured for comparison.

4.2 Experimental Details

The first method of investigation was XTEM. Cross-sections were prepared using a dual-beam focused-ion-beam (FIB) system as detailed in Section 2.3.1. Although sample preparation by FIB is known to induce amorphization of the side walls of the resulting cross-section [138], this method was chosen for the conventional TEM analysis over wet-etching using HF, as the latter was observed to induce crystallization\(^a\). The cross-sections were then probed for the presence of nanocrystals or crystalline cones by careful selected area diffraction analysis and dark-field imaging. The presence of nanopores and voids was studied using conventional bright-field imaging. Additionally, Raman microspectroscopy was used in some cases to confirm the presence or absence of crystallinity.

The surface roughness of the magnetron-sputtered films was investigated using a Nanoscope IIIa atomic force microscope in contact mode. The RMS roughness was calculated using the custom software of the instrument [207].

As detailed in Chapter 3, deposition methods almost always result in the presence of impurities in an amorphous film. Therefore, the argon concentration of some of the magnetron-sputtered films was determined using RBS. Experimental spectra were fitted by simulations from QUARK [208]. Measurements were made with a 2 MeV He\(^+\) beam using the ANU 1.7 MV tandem NEC accelerator employing an Alphatross source. The He\(^+\) ions were axially channelled in the <100> direction to obtain contrast between the amorphous layer and the crystalline substrate. This allows the mass density to be calculated through measurement of the areal density of Si atoms in the amorphous layer. It is not possible however, to measure the hydrogen contents of films using RBS, so other ion-beam techniques need to be employed such as nuclear reaction analysis, forward recoil methods or SIMS. Therefore, some of the PECVD grown and magnetron-sputtered films were analysed together with ion-implanted a-Si for comparison using SIMS. This SIMS analysis was performed by the SIMS Services of the Evans Analytical Group [209].

Lastly, selected films were probed for their mass density using RBS, in conjunction with XTEM, or EELS. In the case of the RBS method, XTEM was used to accurately determine the film thickness and RBS to obtain the number of atoms (cm\(^{-2}\)) in the film. The accurate thickness was then used by the QUARK [208] simulations in order to obtain an estimate of the film’s mass density. This approach was used for the sputtered films. In the case of the PI a-Si however, it was not possible to use RBS due to the very small area of material formed under the indentation tip. Therefore, the mass density of PI a-Si was measured using EELS (as detailed in Section 2.3.4). As discussed previously it is not

\(^a\)This issue of HF induced crystallization resulting from the wet-etching is detailed in Appendix B, Section B.1.
possible to prepare TEM specimens for structural analysis with a FIB system and thus the specimen for the EELS analysis were prepared by the plan-view technique based on back-thinning and wet-etching explained in Section 2.3.1.

4.3 Results and Discussion

4.3.1 Uniformity of PECVD Amorphous Silicon

Several films deposited by PECVD for various lengths of time (as detailed in Section 3.1) were investigated using XTEM. Bright-field images of such cross-sections are shown in Fig. 4.1. The respective selected area diffraction patterns (SADPs) of the films are shown as insets on the right-hand side and dark-field images of interesting features as insets on the left-hand side of the images.

The bright-field image of the film with the nominal deposition time of 6 mins is shown in part (a) of the figure and seems to indicate the presence of a uniform amorphous film. Additionally, the SADP of the film appears to indicate solely a-Si. The hint of crystallinity visible in the SADP is due to crystallinity from the platinum layer as the selected area aperture had to be placed on this layer in order to avoid the influence of the c-Si substrate. However, careful dark-field imaging for which the objective aperture had been placed onto the amorphous ring revealed the presence of some scattered nanocrystals. One of these is shown as an inset. The bright-field image of the film deposited for 18 mins shown in Fig 4.1(b) clearly reveals the presence of cones, one of which is marked with an arrow. Although the SAPD shown as an inset appears again amorphous, the dark-field image of one of these cones reveals them to contain crystalline material. A bright-field image of the film deposited for 30 mins is shown in Fig 4.1(c). Clearly voids (the ‘white’ regions marked by an arrow) can be seen surrounding similar cones as observed in the 18 mins deposition case. Furthermore, the SAPD shown as an inset does not appear fully amorphous any longer. The presence of crystals is clearly confirmed by dark-field imaging as shown in the inset. A dark-field image of the film deposited for 30 mins at an increased substrate temperature is shown in Fig 4.1(d) with an SADP as an inset. The dark-field imaging was performed by placing the objective aperture on the first ring. Clearly both, dark-field image and SADP, reveal the full polycrystallinity of the film. From the dark-field imaging the crystal sizes in this film can be estimated to ∼3-5 nm.

The polycrystalline film deposited at increased substrate temperatures was analysed using SIMS, the spectrum of which is shown in Appendix C, Section C.2. At a depth of 100 nm the SIMS detected a hydrogen content of 17.6±0.1 at.%, an oxygen content of 7.7±0.1 at.% and a carbon content of 2.8±0.1 at.%. The other films are expected to have

---

bPlatinum has a ccp structure with the first d-spacings at 2.27 Å and 1.96 Å [210].
Figure 4.1: Bright-field images of TEM cross-sections prepared from PECVD films deposited at a nominal deposition time of (a) 6 minutes, (b) 18 minutes and (c) 30 minutes. SADPs taken from the deposited films and dark-field images of nanocrystals present within the films are shown as insets in each case. (d) A dark-field image of a PECVD film deposited for 30 minutes at an elevated substrate temperature with an SADP taken from the film as an inset.
Chapter 4: Initial Characterization of the Amorphous Films

a similarly high impurity concentration as these values are very typical for PECVD grown films.

In summary, the films show an increasing volume fraction of crystallinity with increasing deposition time and the film deposited at an elevated substrate temperature was found to be almost purely polycrystalline. Furthermore, these films also contain a large amount of impurities.

Therefore, it was not possible to investigate these films for their structural properties any further. Although their deformation behaviour was studied, such findings are tangential to the main thrust of this work, and hence details of these results will only be presented in Appendix D.

4.3.2 Mass Density and Impurity Content of Magnetron-Sputtered Amorphous Silicon

Magnetron-sputtered films were investigated for their uniformity using a combination of AFM, XTEM, RBS and SIMS. Films were deposited at two different substrate temperatures, room temperature and 300°C as detailed in Section 3.2.

AFM scans were performed on as-sputtered films deposited at room temperature and 300°C. An AFM scan of the film deposited at room temperature is shown in Fig. 4.2 (the scan size was 5 × 5 μm²). Clearly, the film reveals a significant surface roughness and the RMS roughness was calculated using the AFM software [207] to be ∼1.4 nm. The AFM scan of the film deposited at 300°C looked essentially the same and revealed an only slightly decreased RMS roughness of ∼1.2 nm.

An example of a TEM cross-section prepared from the amorphous layer sputtered at

![AFM scan of as-sputtered a-Si deposited at 300°C. The scan area is 5 × 5 μm and the z-scale is marked in the image.](image-url)
300°C is shown in Fig. 4.3. The bright-field image in part (a) of the figure reveals the presence of vertical nanopores within the amorphous layer. These nanopores however, are difficult to see in a printed version of the micrograph and therefore the region marked with a box in (a) is shown in Fig. 4.3(b) with artificially saturated contrast and decreased contrast.

Figure 4.3: (a) Bright-field image of a TEM cross-section prepared from the as-sputtered amorphous film taken with a CCD camera and (b) a close-up of the region marked with a box shown with increased contrast.

Figure 4.4: Bright-field images of TEM cross-sections prepared from (a) an as-sputtered film and (b) an annealed film, both sputtered at 300°C. The dotted line in both cases indicates the surface position used to obtain the average film thickness.
Chapter 4: Initial Characterization of the Amorphous Films

brightness. Some of the nanopores are marked with arrows for clarity.

Additional examples of XTEM micrographs of the as-prepared and relaxation annealed film sputtered at 300°C are shown in Fig. 4.4(a) and (b), respectively. These cross-sections were used to determine the film thickness, whereby an average thickness was determined as marked by the dotted lines due to the surface roughness. The results of these thickness measurements are summarized in Table 4.1.

The films were then investigated for their mass density using RBS. Using the thickness measured by XTEM the mass density was extracted using QUARK [208] and is also summarized in Table 4.1. The RBS spectra together with the simulations are shown in Appendix C, Section C.1. The density was found to be 94.4±4.7% the mass density of c-Si for both cases, with the large error attributable to the surface roughness. The mass densities of as-implanted and relaxed ion-implanted a-Si taken from Custer et al. [23] are shown for comparison in the same table. The density-deficit of the sputtered films as

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>Film Thickness [nm]</th>
<th>Mass Density [% of c-Si]</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-sputtered</td>
<td>475±12</td>
<td>94.4±4.7</td>
</tr>
<tr>
<td>annealed sputtered</td>
<td>483±17</td>
<td>94.4±4.7</td>
</tr>
<tr>
<td>as-implanted</td>
<td>-</td>
<td>98.21±0.13</td>
</tr>
<tr>
<td>annealed implanted</td>
<td>-</td>
<td>98.30±0.07</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison of film thickness measured from XTEM and mass density measured by RBS for magnetron-sputtered a-Si. The mass densities of as-implanted and relaxation annealed ion-implanted a-Si are shown for comparison. These values are taken from Custer et al. [23].

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>Ar Cont. [at. %]</th>
<th>H Cont. [at. %]</th>
<th>O Cont. [at. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-sputtered</td>
<td>2.0±0.1</td>
<td>1.8±0.1</td>
<td>0.9±0.1</td>
</tr>
<tr>
<td>annealed sputtered</td>
<td>2.0±0.1</td>
<td>0.9±0.1</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td>as-implanted</td>
<td>-</td>
<td>≤0.02±0.01</td>
<td>0.005±0.002</td>
</tr>
<tr>
<td>annealed implanted</td>
<td>-</td>
<td>0.03±0.01</td>
<td>0.005±0.002</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison of argon content measured by RBS and hydrogen and oxygen contents at 100 nm depth measured by SIMS for ion-implanted and magnetron-sputtered a-Si. Note the H content in the as-implanted case might be lower as the value quoted is the sensitivity limit of the SIMS.
compared to the voidless ion-implanted case [58] is an indication of nanopores and voids present in the former.

The same RBS measurement was then used to determine the argon content of the films, which yields $\sim 2$ at.% in both cases. The films were further investigated by SIMS for their hydrogen and oxygen contents. All these impurity contents are summarized in Table 4.2. Note that the impurity contents quoted are from a depth of 100 nm and the actual SIMS spectra are shown in Appendix C, Section C.2. Interestingly, the hydrogen content decreases by $\sim 50\%$ upon annealing which is due to the out-diffusion of the hydrogen. In contrast, the oxygen content increases by $\sim 33\%$ which indicates the increase of the thickness of the native oxide on the external as well as internal surfaces. The H and O contents of as-prepared and relaxation annealed ion-implanted a-Si were also measured using SIMS for comparison and are summarized in Table 4.2. However, the H content in the as-implanted case appears to be below the sensitivity limit of the SIMS and thus the content quoted is the upper limit.

In summary, the sputtered films, as-prepared and annealed, are found to be relatively uniform although both have a significant surface roughness. Additionally, both films have a significant density-deficit which can be attributed to the presence of voids and nanopores. Moreover, both films have a total impurity content of $\sim 5\%$ which is considerably higher than for ion-implanted a-Si, but also significantly lower than for the PECVD films. Therefore, these films were sufficiently uniform to be investigated for their structural properties by indentation, Raman microspectroscopy and FEM.

### 4.3.3 Uniformity of Laser-Quenched Amorphous Silicon

The laser-quenched a-Si made as detailed in Section 3.3 was investigated for its structural properties by Raman microspectroscopy and XTEM. Raman microspectroscopy was performed on as-prepared laser-modified (‘as-quenched’) and relaxation annealed zones and the resulting spectra are shown in Fig. 4.5. Both spectra reveal a small a-Si peak as a shoulder on the large Si-I TO peak. Surprisingly, the as-quenched a-Si shows some additional peaks at $\sim 350 \text{ cm}^{-1}$ and possibly at $\sim 460 \text{ cm}^{-1}$. The peak at $\sim 350 \text{ cm}^{-1}$ can be attributed to the high-pressure phase Si-XII, whereas the peak at $\sim 460 \text{ cm}^{-1}$ could be attributed to the high-pressure phase Si-III [95]$.c$ These two phases are the crystalline high-pressure phases usually observed after pressure release from the metallic Si-II phase [82].

A laser-modified spot with a ‘crater’ in the middle was picked for a detailed cross-sectional TEM analysis. Cross-sections were prepared using a dualbeam FIB at varying distances from the edge of the spot since it is well known that a laser-modified zone displays quite different properties across the entire width: polycrystals are observed at the

---

$^c$For details on the Raman spectra of the high-pressure phases refer to Appendix A.
Chapter 4: Initial Characterization of the Amorphous Films

Figure 4.5: Raman spectra of as-quenched and annealed laser-quenched a-Si.

bottom of a ‘crater’ and amorphous areas are observed outside of the crater [179]. An SEM scan of the laser-quenched spot chosen is shown in Fig. 4.6(a). The scan was taken at a tilt of 52° degrees in the dualbeam FIB system prior to milling. An SEM scan from the same spot after the milling of the various cross-sections is shown in Fig. 4.6(b). The cross-sections are labelled by numbers and will be referred to with this number throughout the remainder of this section.

The distances from the edge were measured for all cross-sections and are summarized in Table 4.3. The cross-sections can be grouped into three different types: cross-sections #1, #2, and #3 are very close to the edge of the laser-modified zone and should therefore be mostly amorphous [179]. Cross-sections #4 and #5 were taken from the a-Si zone close to the crater and cross-sections #6 and #7 were taken from within the crater.

Figure 4.6: SEM scans of the as-quenched spot used for the XTEM investigation shown in (a) with 52° degree tilt taken before the milling of cross-sections and in (b) at 0° degree tilt taken after the milling of the cross-sections.
Table 4.3: Distances of the different cross-sections from the edge of the laser-modified zone.

A bright-field image of cross-section #1 (from the first group of cross-sections) is shown in Fig. 4.7(a). The amorphous zone appears quite ‘bubbly’ and large voids can be seen in the layer indicating the non-uniformity of the a-Si layer. An SADP of this amorphous zone is shown in part (b) of the figure. Estimated from the dualbeam FIB preparation the TEM foil is ∼100 nm thick and therefore, distinct a-Si rings would have been expected. The lack of such rings appears due to this large volume fraction of voids. However, the presence of crystalline material is clearly indicated by the reflections visible in the SADP. These reflections correspond to Si-I spacings such as, for example, the reflection at 3.1 Å marked with a box. The additional faint reflections observed at 2.3 Å are most likely due to crystallinity within the platinum layer on top of the cross-section.

Fig 4.7(c) shows a dark-field image whereby the Si-I reflection marked with a box in the SADP had been used for the imaging. The presence of Si-I crystals throughout the a-Si layer is clearly confirmed. Thus, even close to the edge of the a-Si zone, crystals are present within the ‘amorphous’ layer and the amorphous layer is not uniform, but rather seems to consist of ‘bubbles’ of amorphous material with large voids in between.

A bright-field image of cross-section #5 (from the second group) is shown in Fig. 4.8(a). As in the previous case, the amorphous volume appears ‘bubbly’ containing voids. The SADP taken from the amorphous region is shown in Fig. 4.8(b) and quite distinct polycrystalline rings are observed. The d-spacings of the various rings are indicated and labelled in the SADP. The rings at 3.1 Å, 1.9 Å and 1.7 Å can be identified as the \{111\}, \{220\} and \{311\} planes of the diamond cubic Si-I phase, respectively. However, the rings at 4.5 Å, 3.5 Å, 2.3 Å and 2.1 Å cannot be correlated to this phase. Interestingly, the distinct absence of a ring at 2.7 Å also rules out the presence of the high-pressure phases Si-III and Si-XII. Moreover, Si-IV has no d-spacing larger than 3.3 Å and thus has to be ruled out as well. Thus, these polycrystalline rings cannot be attributed to any well characterized phase but may be attributed to the new phase Si-XIII. This latter phase is

---

\[^d\]Platinum has a ccp structure with the first d-spacings at 2.27 Å and 1.96 Å [210].

\[^e\]Refer to Table A.3 in Appendix A for the d-spacings of the various high-pressure phases observed at ambient.
Chapter 4: Initial Characterization of the Amorphous Films

Figure 4.7: (a) Bright-field image, (b) SADP and (c) dark-field image of cross-section #1. The SAPD is taken from the amorphous region observed in the bright-field image and the Si-I reflection used for the dark-field imaging is marked with a box.
Figure 4.8: (a) Bright-field image, (b) SADP and (c) dark-field image of cross-section #5. The SAPD is taken from the amorphous region shown in the bright-field image and the $d$-spacings of the various polycrystalline rings are labelled in Ångstroms. The reflection used for the dark-field imaging is marked with a light blue circle and labelled 4.5 Ångstrom.
Figure 4.9: (a) Bright-field image, (b) SADP and (c) dark-field image of cross-section #7. The SAPD is taken from the polycrystalline region shown in the bright-field image and the \(d\)-spacings of the various polycrystalline rings are labelled in Ångstrom. The reflection used for the dark-field imaging is marked with a dark blue circle and labelled \(4.7\) Ångstrom.
Section 4.3: Results and Discussion

reported to form from Si-III and/or Si-XII after thermal annealing [103, 130]. For further
details on this new phase of silicon refer to Section A.3 of Appendix A.

If the phase observed here is indeed Si-XIII, the rings could be indexed as the \{101\} plane for the ring with 4.5 Å, \{102\} for 3.5 Å, \{200\} or \{201\} for 2.3 Å and \{202\} for 2.1 Å. A dark-field image of this cross-section is shown in Fig. 4.8(c). The reflection used for the dark-field imaging is marked with a dark blue circle in the SAPD and labelled as 4.5 Å. The presence of crystals throughout the top layer is clearly observed and these crystals may have the Si-XIII structure. However, regardless of the exact crystalline structure of these crystals, it is clear that close to the edge of the crater no pure amorphous film is formed.

An example of a cross-section taken from the bottom of the crater is shown in Fig. 4.9. The bright-field image in part (a) reveals large crystals of polycrystalline material with dislocations present within the crystals. An SAPD is shown in Fig. 4.9(b). Some polycrystallinity is indicated by the faint polycrystalline rings although the crystals appear large enough to give a mainly single crystal diffraction pattern. The \(d\)-spacings of the individual rings/reflections are again marked with circles and indicated in the SADP. The single crystal reflections at 3.1 Å, 2.7 Å (double diffraction), 1.9 Å and 1.7 Å can again be attributed to Si-I. However, additional reflections at 4.7 Å and 2.3 Å are observed. These are clearly linked to the presence of the high-pressure phase Si-III as Si-XII does not have a \(d\)-spacing of 2.3 Å. Therefore, these \(d\)-spacings can be attributed to the \{110\} and \{220\} planes of Si-III, respectively. The Si-III reflection at 4.7 Å was used for the dark-field imaging shown in Fig. 4.9(c). In the dark-field image the Si-III crystal is marked with an arrow.

Clearly the region outside of the crater consists of amorphous ‘bubbles’ interspersed with crystallites, whereas the bottom of the crater is fully polycrystalline. Interestingly,

![Figure 4.10: Schematic representation of the laser-quenched spot.](image-url)
some of these crystals are not Si-I but crystalline high-pressure phases. This structure-
zone model is shown schematically in Fig. 4.10. The somewhat surprising presence of
these high-pressure phases is most likely due to the similarities between the molten form
of Si and the metallic phase Si-II. This similarity is explored in more depth in Section E.2
in Appendix E.

In summary, clearly the laser-modified zone is not completely amorphous. Not only
is the laser-modified zone full of voids and the ‘amorphous’ film seems to consist of
individual a-Si ‘bubbles’ rather than a uniform layer, crystals are present throughout the
entire laser-modified zone. Therefore, these films were also not investigated for their
structural properties any further, although their deformation behaviour was studied and is
presented in Appendix E, Section E.1.

4.3.4 Uniformity and Mass Density of Pressure-Induced Amorphous Silicon

The uniformity of the PI a-Si created by spherical indentation with a large indentation tip
(~18 µm radius) was investigated by XTEM. A bright-field image of a cross-section of
such a microindent is shown in Fig. 4.11(a). Clearly a large phase transformed zone can
be observed with slip from the indentation process occurring in the underlying substrate.
Note that this particular cross-section also contains the edge of a nanoindent visible to the
right of the boxed region. Nonetheless, the area of the microindent aside from this nanoindent
can still be investigated for the uniformity of PI a-Si. An SADP of the amorphous
layer was taken from the area indicated by a box in the micrograph and is shown as an
inset. Although some crystallinity presumed to originate from the substrate can be seen,
the SADP appears mainly amorphous. For further investigation, a dark-field image of that
same boxed region was taken by placing the objective aperture on the faint crystalline spot
in the SADP. The resulting dark-field image is shown in Fig. 4.11(b) and reveals clearly
a uniform layer of a-Si with no evidence of void-like structures or nanopores. Lastly, the
PI a-Si was also investigated in plan-view geometry. A bright-field image of an entire
microindent taken with the CCD camera is shown in Fig. 4.11(c). Clearly, a large phase
transformed zone can be observed which proved to be solely amorphous by SADP analy-
sis. Note that the phase transformed zone (i.e. the PI a-Si) is not circular as expected for
a microindent due to non-uniform etching and/or re-crystallization of the PI a-Si.

In some cases however, small volumes of crystalline high-pressure phases can be
found within such a phase transformed zone. This is due to limitations of the UMIS
indentation system with no faster unloading rates possible when performing indentation
with a large tip at room temperature. Thus, the pressure-release rate is slower than for
example for a small spherical tip or a Berkovich tip. Therefore, all microindents were
tested for the presence of such high-pressure phases by Raman microspectroscopy prior
Figure 4.11: TEM micrographs of large spherical indents consisting purely of PI a-Si: (a) bright-field image of the whole indent in cross-sectional geometry, (b) dark-field image of a close-up of the a-Si layer from the region marked with a box and (c) bright-field image of a whole indent in plan-view geometry. Note that the cross-section contains the edge of a nanoindent, but that the SADP shown in part (a) was taken aside from this nanoindent.
to further mechanical testing for example.

The mass density $\rho_0$ of PI a-Si was investigated in detail using EELS and compared with that of ion-implanted a-Si and also c-Si. Therefore, the plasmon-energy $E_p$ of as-indentented and relaxation annealed PI a-Si as well as of as-prepared and relaxation annealed ion-implanted a-Si and c-Si was measured. The plasmon-energy was fitted and used to calculate the mass density. Details for this procedure are given in Section 2.3.4 in Chapter 2.

The averaged plasmon energies and mass densities for each material are summarized in Table 4.4. Additionally, the mass densities from the literature are quoted for comparison. The measurement for the ion-implanted cases is in excellent agreement with the literature thus giving confidence that the determination of mass density by EELS is a reliable measurement. This is noteworthy as the determination of the mass density by EELS is dependent on the effective electron mass $m^*$. Interestingly, the mass density of as-indentented PI approaches that of c-Si to within experimental error, thus making it the most dense form of a-Si measured to date at ambient. A high density for a-Si is not unexpected however, as for example the WWW-model of a-Si has predicted an even higher density of a-Si than for c-Si (see for example Refs. [35, 211]).

Intriguingly, this mass density of PI a-Si decreases significantly upon annealing which is different to what is observed for the case of ion-implanted a-Si (in the latter case the mass density is the same within error). This behaviour might be due to the fact that as-indentented PI a-Si originated from a highly compressed state and thus may be a structurally less stable state of a-Si. The mass density of annealed PI a-Si is even lower than observed for annealed ion-implanted a-Si, the reason for which is not yet entirely clear. One possible explanation could lie in the fact that the mass density is determined from very thin TEM specimens and therefore the majority of the residual stresses present in the bulk PI

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_p$ (Measured) [eV]</th>
<th>$\rho_0$ (Measured) [g/cm$^3$]</th>
<th>$\rho_0$ (from Lit.) [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-implanted</td>
<td>16.61±0.07</td>
<td>2.289±0.010</td>
<td>2.287±0.003 [23]</td>
</tr>
<tr>
<td>annealed implanted</td>
<td>16.62±0.08</td>
<td>2.290±0.012</td>
<td>2.289±0.002 [23]</td>
</tr>
<tr>
<td>as-indented PI</td>
<td>16.74±0.09</td>
<td>2.322±0.013</td>
<td>-</td>
</tr>
<tr>
<td>annealed PI</td>
<td>16.49±0.05</td>
<td>2.255±0.007</td>
<td>-</td>
</tr>
<tr>
<td>c-Si</td>
<td>16.81±0.06</td>
<td>2.343±0.009</td>
<td>2.3290 [157]</td>
</tr>
</tbody>
</table>

Table 4.4: Average plasmon energy and mass density of as-prepared and relaxation annealed ion-implanted and PI a-Si and of c-Si. The known mass densities from the literature are given for comparison.
Section 4.4: Summary

state have been relieved during the sample preparation. This could lead to an expansion of the film and thus an underestimation of the mass density. If this holds true however, it would also imply that the density of as-indented PI a-Si is equally underestimated, a fact which would put ‘bulk’ as-indented PI a-Si at a significantly higher density than c-Si.

In summary, PI a-Si was found to be similarly uniform as ion-implanted a-Si with a mass density approaching that of c-Si. Differently to ion-implanted a-Si however, the mass density was observed to decrease upon annealing.

4.4 Summary

Only the PI a-Si approaches the uniformity of the ion-implanted case. Although some PI a-Si microindents might contain small volumes of high-pressure phases, the majority of the phase transformed zone is crystal-free and no voids are observed. Moreover, the mass density of as-indented PI a-Si approaches or even exceeds the mass density of c-Si. This is clearly due to the mode of formation from a dense metallic phase. Intriguingly, the mass density of as-indented PI a-Si was observed to be significantly higher than c-Si.

Table 4.5: Comparison of mass density, impurity content and uniformity of the different forms of a-Si.

<table>
<thead>
<tr>
<th>Form of a-Si</th>
<th>Mass Density [% of c-Si]</th>
<th>Impurity Cont. [at. %]</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-prepared PECVD</td>
<td>-</td>
<td>≥20</td>
<td>crystallinity</td>
</tr>
<tr>
<td>annealed PECVD</td>
<td>-</td>
<td>≥20</td>
<td>crystallinity</td>
</tr>
<tr>
<td>as-sputtered 300°C deposition</td>
<td>94.4±4.7\textsuperscript{a}</td>
<td>∼5</td>
<td>uniform, but porous</td>
</tr>
<tr>
<td>annealed sputtered 300°C deposition</td>
<td>94.4±4.7\textsuperscript{a}</td>
<td>∼5</td>
<td>uniform, but porous</td>
</tr>
<tr>
<td>as-quenched</td>
<td>-</td>
<td>10^{-9}</td>
<td>voids, nanocrystals</td>
</tr>
<tr>
<td>annealed quenched</td>
<td>-</td>
<td>∼0.04</td>
<td>voids, nanocrystals</td>
</tr>
<tr>
<td>as-implanted</td>
<td>97.6±0.8\textsuperscript{b}</td>
<td>10^{-9}</td>
<td>uniform</td>
</tr>
<tr>
<td>annealed implanted</td>
<td>97.7±0.9\textsuperscript{b}</td>
<td>∼0.04</td>
<td>uniform</td>
</tr>
<tr>
<td>as-indented PI</td>
<td>99.1±0.9\textsuperscript{b}</td>
<td>10^{-9}</td>
<td>uniform</td>
</tr>
<tr>
<td>annealed PI</td>
<td>96.2±0.7\textsuperscript{b}</td>
<td>∼0.04</td>
<td>uniform</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Determined by RBS.  
\textsuperscript{b}Determined by EELS.
density of PI a-Si decreases upon annealing which is different to what is observed for ion-implanted a-Si. Additionally, the PI a-Si is expected to be as impurity free as the c-Si it is formed from. Thus, the hydrogen content, for example, is expected to be in the order of $10^{12}$ cm$^{-3}$ [212]. Some in-diffusion of hydrogen is expected to occur upon annealing, but not more than observed for annealed ion-implanted a-Si. Compared to these pure cases of a-Si, deposited a-Si contains a significant amount of impurities. An overall content of $\sim 5$ at.$\%$ is observed for the sputtered a-Si. No evidence of crystallinity is observed in this case however, making it a uniform film despite the evidence of porosity. In contrast, both the laser-quenched and the PECVD films were found to be non-uniform both containing significant volume fractions of crystallinity. All these findings are summarized in Table 4.5.

These various forms of a-Si, with their different uniformity, impurity contents, crystallinity fractions and mass densities were to be investigated in detail for their mechanical properties as well as their medium- and short-range order characteristics. The PECVD and laser-quenched films however, cannot be investigated for their structural properties due to the lack of uniformity and thus the details of these films do not significantly contribute to the framework for the understanding of a-Si that is to be developed in this thesis. Although these films were probed for their deformation behaviour, since this process seems to be particularly sensitive to the ‘state’ or ‘structure’ of the a-Si, the detailed results from these findings are given in the appendices.

The more uniform films (i.e. magnetron-sputtered, ion-implanted and PI) are investigated for their indentation-induced deformation behaviour and also their indentation hardness. These films are then studied by FEM as this technique requires relatively large areas of uniform thickness. Moreover, only the pure forms of a-Si (i.e. ion-implanted and PI) are investigated for their short-range order characteristics using electron diffraction as the presence of impurities can complicate the interpretation of RDFs significantly. All three uniform films however, are studied for their short-range order characteristics using Raman microspectroscopy. The results from these characterizations will be presented in the next chapters.