ON THE SOLID PHASE CRYSTALLISATION FOR THIN FILM SILICON SOLAR CELLS ON GLASS

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FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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2013
DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

__________________
Felix Law

First submission: 31 May 2013
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ACKNOWLEDGEMENTS

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Not forgetting the people who have supported me since the early days: Jiaji, Linfen and Jenny. Thanks for your kind advice and support throughout all these years. I am so glad to have you around. Jenny, you will be dearly missed.

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Finally, thanks to my family for the unwavering support and for bringing laughter and joy to my life.

This journey has been fun, thanks to you all.
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SUMMARY

Polycrystalline silicon (poly-Si) thin films have potential for low cost photovoltaic applications. Fabrication of poly-Si thin films involves the deposition of a hydrogenated amorphous silicon (a-Si:H) thin film followed by the solid phase crystallisation (SPC) process, where the a-Si:H film is crystallised at > 550 °C into poly-Si. However, the SPC process for the poly-Si thin film solar cell technology is not well understood as evidenced by the high density of defects within the poly-Si materials. With focus on material properties, this Thesis is concerned with enhancing the understanding of the SPC process for poly-Si thin film solar cells on glass by investigating the precursor a-Si:H material properties, the SPC dynamics and the final poly-Si material quality.

Work in recent years suggest that the a-Si:H material is anisotropic in nature. Nucleation sites can be defined by localised regions within the a-Si:H which have higher degree of ordering and tend to crystallise more readily compared to other regions of the a-Si:H material. Results suggest that the average grain size in a poly-Si film is not solely affected by the SPC kinetics and the number density of these nucleation sites may play a role. Different a-Si:H films may inherently have different densities of nucleation sites, resulting in different average grain sizes.

Medium range ordering (MRO) is a term used to describe the structural ordering of a-Si:H on a medium range length scale (up to 5 nm). Results showed that a-Si:H films demonstrating reduced MRO resulted in better poly-Si material. Lowering of the MRO can be achieved by reducing the deposition pressure and our results indicate that ion bombardment may play a role in controlling MRO.

Geometrically necessary dislocations (GNDs) were identified in poly-Si and found mainly in grains which are > 3 µm. GNDs can form in response to stress on the poly-Si material
during the SPC process and results indicate that the grain size may be correlated to the GND formation in the poly-Si material. Stress may have built up within the system during SPC since denser poly-Si inclusions form within the less dense a-Si:H matrix and material continuity is maintained between the two phases. To gain further insights, attention was turned towards the behaviour of the a-Si:H during the SPC process. It was interesting to note that the root mean square bond angle in a-Si:H increasingly deviates from the ideal Si bond angle of $109.5^\circ$ with the crystal fraction. In addition, FTIR also revealed a changing Si-Si bond polarisability with the crystal fraction. These observations are not completely understood but they may be essential to understanding stress formation in SPC poly-Si and to eventually minimise dislocation incorporation during the SPC process.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( f )</td>
<td>Fraction of crystallinity</td>
</tr>
<tr>
<td>( k )</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Lattice curvature</td>
</tr>
<tr>
<td>( n_0 )</td>
<td>Avrami exponent</td>
</tr>
<tr>
<td>( n )</td>
<td>Apparent Avrami exponent</td>
</tr>
<tr>
<td>( N )</td>
<td>Nucleation rate</td>
</tr>
<tr>
<td>( Q )</td>
<td>UV reflectance structural quality factor</td>
</tr>
<tr>
<td>( R^* )</td>
<td>Microstructure factor</td>
</tr>
<tr>
<td>( S )</td>
<td>Shape factor</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
</tr>
<tr>
<td>( T_m )</td>
<td>Melting temperature of silicon (1414 °C)</td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
</tr>
<tr>
<td>( t_c )</td>
<td>Characteristic time of solid phase crystallisation</td>
</tr>
<tr>
<td>( t_0 )</td>
<td>Incubation time for solid phase crystallisation</td>
</tr>
<tr>
<td>( \theta_M )</td>
<td>Misorientation angle</td>
</tr>
<tr>
<td>( \Delta \theta )</td>
<td>Short range order bond angle distortion</td>
</tr>
<tr>
<td>( \nu_g )</td>
<td>Growth rate</td>
</tr>
</tbody>
</table>
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>3-D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>a-Si</td>
<td>Amorphous silicon</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>Hydrogenated amorphous silicon</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>C_H</td>
<td>Hydrogen content</td>
</tr>
<tr>
<td>c-Si</td>
<td>Crystalline silicon</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
</tr>
<tr>
<td>ETP</td>
<td>Expanding thermal plasma</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Tranform Infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>GAM</td>
<td>Grain average misorientation</td>
</tr>
<tr>
<td>GND</td>
<td>Geometrically necessary dislocation</td>
</tr>
<tr>
<td>HAADF-STEM</td>
<td>High angle annular dark field scanning transmission</td>
</tr>
<tr>
<td></td>
<td>electron microscopy</td>
</tr>
<tr>
<td>HSM</td>
<td>High stretching mode</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>JMAK</td>
<td>Johnson-Mehl-Avrami-Kolmogorov</td>
</tr>
<tr>
<td>KAM</td>
<td>Kernel average misorientation</td>
</tr>
<tr>
<td>LAGB</td>
<td>Low angle grain boundary</td>
</tr>
<tr>
<td>LID</td>
<td>Light induced degradation</td>
</tr>
<tr>
<td>LSM</td>
<td>Low stretching mode</td>
</tr>
<tr>
<td>MRO</td>
<td>Medium range order</td>
</tr>
<tr>
<td>NMR</td>
<td>Nucleation magnetic resonance</td>
</tr>
<tr>
<td>Poly-Si</td>
<td>Polycrystalline silicon</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>RF-PECVD</td>
<td>Radio Frequency parallel plate Plasma Enhanced</td>
</tr>
<tr>
<td></td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid thermal annealing</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small angle X-ray scattering</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SiN_x or a-Si_N_y_H_z</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>SPC</td>
<td>Solid phase crystallisation</td>
</tr>
<tr>
<td>SRO</td>
<td>Short range order</td>
</tr>
<tr>
<td>SSD</td>
<td>Statistically stored dislocation</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

In this chapter, the advantages of photovoltaics are discussed and a review of the different thin film solar cell technologies is given. An introduction of the polycrystalline silicon thin film solar cell technology is given as well.
1.1 The need for renewable energy

There are two main motivations for adopting renewable energy – climate change and building a sustainable energy system. Fossil fuels (coal, oil and gas) are still the major sources of energy in the world today, providing about 80% of the world’s energy in 2010 [1]. The burning of fossil fuels releases CO₂ into the atmosphere thereby contributing to global warming. Moving away from these fossil fuels is not straightforward, considering that fossil fuels are so convenient and reliable and the infrastructure for today’s energy system is so well established. Fossil fuels have driven economic growth from the industrial revolution, which in turn encourages more extraction of fossil fuels: this is a vicious cycle.

Climate change aside, there is also the issue of energy security. Disruption in the fossil fuel supplies can be caused by conflicts, natural disasters or technical failures. Especially in countries relying on imports of the fossil fuels, energy security is a pressing issue. Renewable energy sources can provide a solution in this matter as almost every country in the world has a certain renewable energy potential.

While renewable energy sources are desirable, it currently still requires government support and subsidies to compete with fossil fuels. This is partly due to the fact that “externalities” such as climate change, decommissioning costs, subsidies, health risks, waste, etc., are currently not priced into fossil and nuclear energy: a “real” pricing would significantly increase the cost (and price) of fossil and nuclear energy.

Solar energy potential far exceeds those of other renewable energy resources, such as biomass, wind and hydro power, which are in fact energy sources derived from solar energy [2]. There is no silver bullet for achieving a sustainable energy system and all forms of renewable energy sources will very likely play a role. The solar energy source is
huge compared to our current energy needs, however only a very small portion of this energy source is tapped. According to the International Energy Agency (IEA), it is estimated that 885 million terawatt hours (TWh) reach the earth’s surface in a year, which is 6200 times the world energy consumption in 2008 [2]. In other words, the Sun takes 85 minutes to send the same amount of energy to earth that the world consumes in a year [2].

Photovoltaic (PV) cells or solar cells are an attractive technology to tap into the enormous solar energy source, where solar energy is directly converted into a very high quality fuel (electricity) without intermediate steps. In addition, solar cell technology is a proven technology which is robust and long lasting.

1.2 Thin film solar cells

Si wafer technology currently dominates the PV industry because it is a proven and well understood technology. However, the process to turn sand into Si wafers is energy intensive. SiH₄ or SiHCl₃ are used in the Siemens process to produce Si feedstock which is molten at 1414 °C and cooled slowly to recrystallise into Si ingots. The Si ingots are then wire sawed into Si wafers and in this process Si material is wasted as Si saw dust. The Si wafers are typically 160 µm thick for easy handling and a typical Si wafer solar cell uses more Si material than it actually requires for light absorption. A method to potentially reduce the cost is to change the Si wafer production process and to reduce the amount of active material. Having a very thin film requires a substrate to provide mechanical support. Glass [3] and metal foils [4, 5] are candidates, while plastic substrates may be explored as well, they are less popular due to low temperature tolerance. This leads us to the concept of thin film solar cells. Thin film technologies comprises of copper indium gallium di-selenide (CIGS), cadmium telluride (CdTe) and silicon based thin film solar cells; which include hydrogenated amorphous silicon (a-Si:H),
microcrystalline silicon (µc-Si), micro-morph tandem silicon and polycrystalline silicon (poly-Si) thin film solar cells. CIGS and CdTe thin film solar cells are plagued by the scarcity of indium and tellurium, respectively [6], which could potentially lead to increase in production cost in the future. Silicon based thin film solar cells on the other hand do not have issues with the availability of raw materials since silicon is the second most abundant material on earth. In addition, Si is non-toxic unlike cadmium [7]. Therefore silicon based thin film solar cells are highly desired.

The a-Si:H thin film solar cell technology is attractive for low-cost PV applications because of a high optical absorption coefficient, allowing very thin absorber layers of < 300 nm [7]. Large area radio frequency parallel plate plasma enhanced chemical vapour deposition (RF-PECVD) at relatively low temperature of ~200 °C is possible as this technology benefits from the developments of deposition systems for liquid crystal displays. The a-Si:H thin film solar cell is less successful in the market because of low efficiencies brought upon by light-induced degradation (LID). While efficiencies of > 10 % can be achieved at laboratory scale, stabilised efficiencies for production is typically only 7% or less [7].

The µc-Si thin film technology is attractive because relatively higher grade silicon material can be obtained at low temperatures (200 °C) using very high frequency (VHF, > 13.56 MHz) variant of the RF-PECVD technique. In addition, these cells do not suffer from extensive LID as compared to a-Si:H thin film solar cells. However, due to the low deposition rates (< 40 nm/min) and the difficultly in scaling up VHF RF-PECVD systems, this technology is not easy to commercialise. Laboratory scale devices of > 10% were realised for this technology [8].
By combining a-Si:H and µc-Si thin films into a tandem structure, the micro-morph thin film solar cell concept was first introduced by the University of Neuchatel in the 1990s [9]. Due to the difference in band gap between a-Si:H and µc-Si (1.7 eV and 1.0 eV, respectively), a better utilisation of the solar spectrum can be achieved, leading to higher conversion efficiencies. A record pre-stabilised efficiency for this technology is 14.5% (with a cell area of 1 cm²) [10]. The drawbacks of this technology follow that of the single junction µc-Si thin film solar cell technology.

Of the different silicon based thin film technologies, poly-Si thin film is chosen as the area of study because it is not plagued by LID [3] and it benefits from the developments of the 13.56 MHz RF-PECVD technique used in the deposition of thin film transistors in the active matrix liquid crystal display industry, where RF-PECVD on glass sheets up to 9 m² (Generation 10 deposition equipment) is available in the market [11]. Poly-Si thin film solar cells based on the solid phase crystallisation (SPC) of a-Si:H was pioneered by Sanyo in the 1990s, where they reached a solar cell efficiency of 9.7% [4, 12-14]. It was interesting to note that no post-SPC treatment, such as rapid thermal annealing (RTA) or hydrogenation, was reported by Sanyo. The world record efficiency of 10.5% was achieved by CSG solar on a 20-cell mini-module of 94 cm² [15, 16]. Other than the SPC method, there are other methods to fabricate the poly-Si active layers, such as using aluminium induced crystallisation (AIC) of a-Si:H to first form a seed layer and epitaxially thickening the seed layer using deposition methods, such as thermal CVD [17-20] or ion assisted deposition [21]. Highest efficiency obtained for the poly-Si thin film solar cells by this fabrication method is 8% reported by IMEC [20].

Recently, the NREL group introduced hot wire chemical vapour deposition (HWCVD) epitaxial growth of poly-Si thin film materials on a proprietary metal foil substrate – roll assisted bi-axially textured substrate (RABITS). HWCVD is capable of reaching
deposition rates of > 300 nm/min [5]. The heating and rolling processes create a uniform and highly oriented cubic crystal substrate. Buffer layers were used between the substrate and the deposited c-Si film. NiW foil substrates were explored and the buffer layers used were MgO, $\gamma$-Al$_2$O$_3$ or $\alpha$-Al$_2$O$_3$. The buffer layers provide a compatible crystalline order for good hetero-epitaxial growth and also to act as an impurity barrier between the c-Si film and the substrate [22]. In 2007, Ampulse Corporation, a spin-off company based on this technology was formed. So far a test device with an open circuit voltage of 580 mV was achieved on a sapphire “model template” for Al$_2$O$_3$, which is promising since the record open circuit voltage of crystalline silicon thin film solar cell devices was previously ~550 mV.

Another method for fabrication of poly-Si thin films is the crystallisation of a-Si:H thin films using lasers. In the display industry, pulsed laser crystallisation of a-Si:H is well established for obtaining poly-Si thin film transistors suitable for flat panel display applications. Advantages of pulsed laser crystallisation include faster processing time compared to SPC and minimal damage to the supporting glass substrate [23]. However, there were no promising results reported for poly-Si thin film solar cells based on the pulsed laser crystallisation method. On the other hand, Dore et al. [24, 25] reported 11.7% poly-Si thin films solar cell device (1 cm$^2$) using continuous wave laser crystallisation of a-Si:H.

The SPC method is adopted and is the focus of this work. Figure 1.1 shows the schematic of a poly-Si thin film solar cell structure used at Solar Energy Research Institute of Singapore (SERIS), where this work was carried out. The contacting scheme is beyond the scope of this Thesis and is represented here in a simplified form. The solar cell design adopts a superstrate configuration where the sunlight enters the cell through the glass substrate. For more efficient light utilisation, the glass substrate can be
textured and it can be done by different methods. In the case of CSG solar [3], coating of silica beads on the glass substrate as well as abrasion-etch texturing were employed. Recently, an aluminium induced texturing (AIT) method was developed and found to be compatible with poly-Si solar cells, and solar cells with an efficiency up to 9.3% were realised [26, 27]. The AIT method is adopted at SERIS. Textured substrates are beyond the scope of this thesis and readers are referred to reference [28] for more details. Silicon nitride (SiNₓ) acts as an impurity diffusion barrier from the glass as well as an anti-reflective coating. The SiNₓ layer is kept identical throughout this research project. The front surface region is n⁺ doped and the back surface region is p⁺ doped, with typical doping concentrations of 10¹⁹ – 10²⁰ cm⁻³. The front and back surfaces are heavily doped and directly contacted as shown in Figure 1.1. No transparent conducting oxides (TCOs) are required in this solar cell design since the lateral conductance of the doped layers is sufficient, hence saving cost and processing time. The solar cell shown in Figure 1.1 is p-type based, but n-type based poly-Si has been demonstrated to work as well. For example, Sanyo [4] achieved 9.7% solar cell efficiency (1 cm²) for an n-type based poly-Si solar cell. Typical base doping levels are in the range of 10¹⁵ – 10¹⁶ cm⁻³.
Figure 1.1. Schematic of poly-Si thin film solar cell structure utilised at SERIS.

Figure 1.2 shows the main process fabrication steps used at SERIS for poly-Si thin film solar cells. First the glass substrate is cleaned and textured followed by the deposition of SiNₓ. Subsequently the different doped layers are deposited in the sequence shown in Figure 1.1. Then the sample is subjected to the solid phase crystallisation (SPC) process, where the a-Si:H crystallises to poly-Si. This SPC process takes place under a N₂ ambient or vacuum at a temperature of ~600 °C in a furnace. After crystallisation, the poly-Si material goes through the RTA step (700 – 1000 °C for one minute) for dopant activation and point defect annealing [29]. The grain boundaries are then passivated by the hydrogenation step, where the poly-Si material is exposed to atomic hydrogen generated by plasma at temperatures of 400 – 500 °C [29-31]. Finally the front and rear contacts are formed.
Figure 1.2. Process flow for the fabrication of poly-Si thin film solar cell at SERIS.

Recent advances in understanding poly-Si based thin film solar cells suggest that intra-grain defects are performance limiters [30, 32, 33]. While dangling bonds at grain boundaries are detrimental to solar cell performance as well, they can be minimised by increasing the grain size (lower grain boundary density) as well as passivated by the hydrogenation process. Intra-grain defects can be in the form of dislocations, intra-grain boundaries (such $\Sigma 3$ grain boundaries and twins) or point defects which form during the SPC process.

It is well known that dislocations in silicon are electrically active (reduces minority carrier lifetime) [34, 35] and electrical activity of dislocations has been demonstrated by electron-beam induced current (EBIC) scans. In addition, it has been reported that
metallic impurities, such as Cu, Ni, Fe, Au, Al further enhance the electrical activities of dislocations [33, 34, 36, 37].

Intra-grain boundaries (including twins) are low energy boundaries which form readily during SPC. Since perfect tetrahedral Si bonding is maintained across these boundaries, they are originally electrically inactive. However it has been shown that impurity gettering of Fe and Al at these boundaries can cause them to be electrically active as well [33, 37]. With impurity control during processing, electrical activity at intra-grain boundaries can be minimised.

Point defects are atomic scaled and may include vacancies, interstitial atoms, atoms in the wrong site and presence of impurity atoms. Point defects have low enough formation energies to be formed by thermal activation [38]. At any temperatures, there exists an equilibrium concentration of native point defects (vacancies or interstitial atoms) [39]. Native point defects are used to describe point defects involving only Si atoms while point defects involving impurity atoms, such as P or B dopants, can be referred to as foreign point defects [39]. RTA has been known to anneal point defects and has been used extensively in poly-Si based thin film solar cells [29, 32, 40-43].

Dislocations on the other hand are harder to annihilate since high temperatures are required, which is not possible with glass substrates. Bertoni et al. observed no dislocation density reduction from annealing silicon ribbons at 1100 °C for 6 hours, while above ~1230 °C, dislocation density reduction starts occurring, with up to 95% dislocation density reduction within 60 minutes at a temperature of 1366 °C [44]. Pairwise dislocation annihilation mechanism was proposed as the dominant mechanism over the surface annihilation mechanism based on the dislocation density reduction kinetics, where an activation energy of 2.1 ± 0.2 eV was extracted [44]. It was suggested
that at high enough temperatures, dislocation motion is not constrained by glide planes and dislocations can move freely, facilitating the pairwise dislocation annihilation mechanism [44].

Due to temperature limitations from the glass, post-SPC dislocation engineering via thermal treatments in poly-Si thin film material is hard to achieve. Hence it is desirable to minimise the dislocation incorporation during the SPC process. The SPC process is not completely understood and well controlled, hence developing better understanding of the SPC process is the main goal of this Thesis. Hence, the focus of this Thesis will be mainly on intrinsic films to build fundamental understanding of the SPC process. In Chapter 2, a review of the current understanding of the SPC process will be discussed and therein the theoretical framework for the remainder of the Thesis will be presented.

Knowledge gaps will be identified and followed by an overview of the Thesis.

References


Chapter 2 Theoretical Framework and Overview of Thesis

A theoretical framework which guides the research in this Thesis is presented in this chapter. A review of the solid phase crystallisation (SPC) process is given. The crystallisation model based on the anisotropic amorphous silicon structure is discussed as well. Finally, knowledge gaps are identified and the overview of this Thesis is presented.
2.1 The solid phase crystallisation process

The solid phase crystallisation (SPC) process typically involves annealing an amorphous silicon (a-Si:H) thin film in a N₂ ambient or in vacuum at temperatures of ~600 °C for a duration of more than 10 hours. The deposition of the a-Si:H films is typically done using chemical vapour deposition (CVD) methods which will be covered in Chapter 3. SPC can be broken down into three processes, namely, nucleation, growth and impingement. It should be noted that during SPC these three processes may happen together at any one time.

The SPC process is a phase transformation process where the temperature and pressure are assumed to be constant. For the remainder of this chapter, it is convenient to refer to the amorphous silicon phase and the crystalline silicon phase as a-Si and c-Si, respectively.

A phase is defined as a region within a system whose properties are homogeneous and distinct from the other parts of the system. The reason why phase transformation occurs is because the initial phase is unstable relative to the final phase. The phase stability is determined by the Gibbs free energy for transformation that occurs at constant temperature and pressure [1]. The phase transformation occurs spontaneously such that the Gibbs energy of the system is minimised. The Gibbs free energy of a system is given by

\[ G = H - TS \]  \hspace{1cm} (2.1)

where \( H \) is the enthalpy, \( T \) is the absolute temperature and \( S \) is the entropy of the system. Enthalpy is a measure of heat in the system and is given by

\[ H = E + PV \]  \hspace{1cm} (2.2)
$E$ is the internal energy of the system, $P$ is the pressure and $V$ is the volume. In condensed systems such as liquids and solids, the term $PV$ is very small compared to $E$ and hence in the case of SPC, $H \approx E$. The internal energy of the system consists of the kinetic and potential energy of the system. Kinetic energy arises from the atomic vibrations while potential energy arises from the bonding between the atoms. Most phase transformation processes have an activation barrier and in the case of SPC, this activation barrier may be related to bond breaking and rearrangement between Si atoms and the formation of an intermediate amorphous silicon state [2, 3].

**Figure 2.1** shows the schematic of the Gibbs energy variation during phase transformation. The initial state is $G_1$ and the final state is $G_2$. The initial state $G_1$ corresponds to a local minimum of free enthalpy. The driving force of the transformation is $\Delta G$ and the activation energy barrier is $\Delta G^a$.

![Figure 2.1. Schematic illustration of Gibbs energy during the phase transformation. The initial state is $G_1$ and the final state is $G_2$. The driving force of the transformation is $\Delta G$ and the activation energy barrier is $\Delta G^a$.](image-url)
According to kinetic theory, a higher activation energy barrier leads to a slower rate of phase transformation [4]. For a-Si at room temperature, the phase transformation does not proceed within a reasonable amount of time and it thus appears as a meta-stable state. Only at elevated temperatures of ~600 °C the transformation process completes in 10 - 20 hours.

The kinetics of phase transformation can be described by the Arrhenius rate equation:

\[ \text{rate} \propto \exp\left(-\frac{\Delta G^a}{kT}\right), \]

where \( k \) is the Boltzmann constant. Nucleation and growth are the more important processes and will be discussed in the following sections.

2.1.1 Nucleation

The nucleation process during SPC is the formation of a stable c-Si phase within a relatively less stable a-Si parent phase. Both homogeneous and heterogeneous nucleation will be treated here. For homogeneous nucleation, statistical fluctuations lead to the formation of the c-Si phase. The Gibbs free energy in the system is reduced for every atom transformed from the a-Si phase to the c-Si phase. However, an energy penalty is imposed for the formation of an interface between a-Si and c-Si which increases the Gibbs free energy of the system. Therefore a situation where the volume effect competes with the surface effect is realised. For small clusters of new c-Si phase, the surface effect dominates and the clusters are unstable and tend to dissolve back to the a-Si phase. These unstable clusters are known as germ nuclei. For clusters above a certain critical size \( r^* \), the volume effect dominates and the clusters stabilise. These stable clusters are known as growth nuclei. The Gibbs energy change associated with a cluster of size \( r \), is the sum of the negative volume term and the positive surface term. The change in Gibbs energy associated with a cluster of size \( r \) is given by
\[ \Delta G_r = A \gamma - V \Delta G_V \]  
(2.4)

where \( A \) and \( V \) is the interface surface area and volume of the cluster, respectively. \( \gamma \) is the Gibbs energy increase due to the creation of an interface with area \( A \) and \( \Delta G_V \) is the Gibbs energy decrease due to the formation of a cluster of new phase with volume \( V \). In addition, since the system is in solid state and the silicon material shrinks upon transforming from a-Si to c-Si phase (c-Si has a higher density, hence occupies a smaller volume), a misfit strain energy term \( \Delta G_s \) should be included in Eq. (2.4), resulting in

\[ \Delta G_r = A \gamma - V \Delta G_V + V \Delta G_s \]  
(2.5)

For heterogeneous nucleation, nucleation occurs preferentially at certain sites such as excess vacancies, inclusions, dislocations, grain boundaries, stacking faults and free surfaces. Preferential nucleation at one of these sites results in the destruction of a defect where some free energy (\( \Delta G_d \)) will be released, hence reducing the activation energy barrier. In the case of SPC, preferential nucleation sites can also be localised in regions of higher ordering within a-\( \text{Si:H} \) which crystallises with a lower activation energy barrier. For heterogeneous nucleation, the change in Gibbs free energy associated with a cluster of size \( r \) is given by

\[ \Delta G_{\text{het}} = -V \left( \Delta G_V - \Delta G_s \right) + A \gamma - \Delta G_d \]  
(2.6)

\( \Delta G_d \) can be considered the reduction in nucleation activation energy barrier due to heterogeneous nucleation sites.

**Figure 2.2** shows the schematic diagram of the competition between the volume and surface effects as a function of cluster size.
Figure 2.2. Schematic showing the change in Gibbs free energy of the system associated with a cluster with size $r$. For clusters larger than a critical size $r^*$, volume effect takes over and the overall change in Gibbs free energy associated with that cluster starts to decreases for further increase in $r$.

The time-independent nucleation rate (for both homogeneous nucleation and heterogeneous nucleation) can be defined as the rate of formation of critical sized clusters and is given by

$$N \propto \exp\left(-\frac{\Delta G^*}{kT}\right)$$

(2.7)

where $\Delta G^*$ is the activation energy barrier for nucleation, where it is lower for heterogeneous nucleation. More advanced discussion of nucleation theory can be found elsewhere [5].

2.1.2 Growth

It is important to realise that the SPC system is a single component system, where the single key element is Si. For single component systems, there are no concentration
gradients involved and hence no long range diffusion driven by concentration gradients. Therefore for SPC, the growth of the c-Si is interfacial limited, where the rate of growth is limited by the rate of Si atoms crossing the a-Si/c-Si interface. Non-constant growth rates are typically expected for diffusion limited growth where concentration gradients are a function of time. For interfacial limited growth mechanism, the growth rate is therefore expected to remain constant as SPC proceeds [6]. However it is to be noted that it is possible for growth rates to be non-constant if the material is anisotropic, e.g. due to thermal and/or stress gradients within the material.

2.2 The Avrami exponent

In the literature, the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model has been used to study the SPC dynamics. The general form of the JMAK equation is given by

\[ f(t) = 1 - \exp(-SNV_g^A t^{n_0}), \tag{2.8} \]

where \( S \) is the shape factor, (e.g. \( \pi / 3 \) for spherical growing grains,) \( N \) and \( V_g \) the nucleation and growth rates, respectively. Both \( N \) and \( V_g \) may be time-dependent. The constant \( A \) can have a value of between 2 and 3, where the values of 2 and 3 correspond to a 2 dimensional (2-D) and 3 dimensional (3-D) growth mode for the grains, respectively. In real cases, there can be a mix of 2-D and 3-D growth modes during SPC and the \( A \) value can be between 2 and 3. The parameter \( n_0 \) is known as the Avrami exponent. Different values of \( n_0 \) are reported in the literature and may represent different phase transformation scenarios, provided that strict conditions are met. Some of the commonly stated boundary conditions for application of the JMAK model include:

1) Isothermal and isobaric annealing;
2) Uniform and random nucleation;
3) The growth of the new phase is equal in all directions;
4) Growth rate is time-independent;
5) Growth stops at points of impingement but continues at regions of the same grain where there are no impingements;
6) Nucleation is uniformly distributed spatially.

In the case of the SPC of a-Si:H, however, the phase transformation process is not completely understood and conditions may vary with different samples. Due to the complexity of the SPC process, adherence to the above listed conditions is unlikely and the interpretation of the $n$ values will be ambiguous and should be treated with extreme care. The considerations that may potentially affect the $n$ values for the SPC process of a-Si:H are mainly related to the non-uniform stress and/or thermal distribution within the film which may lead to:

1) Non-constant growth and nucleation rates;
2) Non-uniform spatial distribution of nucleation events with the film;
3) Growth rates of a growing grain not equal in all directions.

While the interpretation of the Avrami exponents is ambiguous, we will show in Chapter 4 that the Avrami exponent can be empirically useful for grouping of different types of a-Si:H materials based on their SPC behaviour and their subsequent poly-Si material morphology. Hence in this Thesis, the Avrami exponent will still be extracted from the SPC dynamics and will be used empirically. The extracted Avrami exponent to be used empirically will be referred to as the *apparent Avrami exponent* from now on and represented by the symbol $n$.

$f(t)$ can be measured experimentally and by linearising Eq. (2.8), $n$ can be extracted via

$$Log \left[ \frac{1}{1 - f(t)} \right] = n \log \left( \frac{t}{t_N} \right) + \log C. \quad (2.9)$$
By plotting $\log \ln \left(\frac{1}{1 - f(t)}\right)$ against $\log t$, the slope gives the $n$ value. $t_N$ is a normalising constant of 1 s and $C$ is a constant.

Figure 2.3a shows the SPC dynamics $f(t)$ extracted from in-situ X-ray diffraction measurements (XRD, to be discussed in more details in Chapter 3) and Figure 2.3b shows the corresponding plot of $\log \ln \left(\frac{1}{1 - f(t)}\right)$ against $\log t$. Figure 2.3b shows a slope of $n = 3.0$.

2.3 Structural model of a-Si:H for SPC

Earlier structural models for a-Si:H were described by the classical random network model [7], where the a-Si:H was thought to be an isotropic random network of Si, containing a homogeneous distribution of dangling bonds as well as bonds terminated by H atoms. In recent years, the view of the a-Si:H structure has changed to an anisotropic network model, containing not just isolated H but also clusters of H decorating mono- or di-vacancies, as well as H decorating the inner surfaces of nano-
voids [8-14]. The presence of H clusters and isolated H are detected by H nuclear magnetic resonance (H NMR) [14-17] while the presence of nano-voids are detected by small angle X-ray scattering (SAXS) [18]. **Figure 2.4** shows the proposed schematic representation of H clusters present in a-Si:H [8, 11, 19].

![Figure 2.4. Schematic drawing of a mono-vacancy (left) and a di-vacancy (right) decorated by H clusters in a-Si:H. Small solid spheres and large solid sphere represent H atoms and Si atoms, respectively. Vacancies are labelled as “v”.](image)

Most of the work on a-Si:H found in the literature is geared towards applications for thin film a-Si:H based thin film solar cells and limited work [14, 20-23] is available that focuses on the use of a-Si:H as the precursor for poly-Si. Nevertheless, recent advances in understanding of the a-Si:H structure in the literature could still be useful for understanding of the SPC process. With the help of the anisotropic a-Si:H structural model and the concept of critical cluster size (see Section 2.1.1), nucleation sites in a-Si:H were identified recently by Mahan *et al.* [14]. A simple anisotropic model is shown schematically in **Figure 2.5**. Only the H distribution is shown, with the H atoms in two configurations, namely, clustered and isolated. The clustered H atoms are in shaded circles while the isolated H atoms are in dashed circles. Nano-voids were found to be not strongly affecting the SPC process, while the distribution of H clusters help to define the location of the nucleation sites.
Figure 2.5. Schematic of the anisotropic a-Si:H structure showing only the distribution of H atoms in clustered and isolated configurations. The clustered H atoms are in shaded circles, while the isolated H atoms are in the dashed circles. The non-clustered regions are relatively well ordered a-Si:H and proposed to be nucleation sites by Mahan et al.[14].

The ratio of clustered to isolated (C/I) hydrogen was extracted via H NMR. The H content (C_H) was measured by Fourier Transform Infrared (FTIR) spectroscopy. With C/I and C_H known, the size of the dashed circle can be estimated since the linear distance between the clusters has an inverse relationship with the cluster density [24] and the linear distance between the H clusters can be taken as the diameters of the dashed circles. The dashed circles represent regions with isolated H which have a better medium range ordering (MRO, up to the scale of 5 nm). The regions with clustered H having worse MRO than regions with isolated H have been shown by X-ray scattering results [14, 17, 25] and is related to H disrupting the Si network in a-Si:H. The average size of the isolated H regions was compared with the critical size for a stable nucleus (calculated to be 44 atoms [26]) and a good correlation was found between the incubation time and the average size of the isolated H regions. The incubation time was
significantly longer if the average size of the isolated H regions was smaller than the critical size and the incubation time quickly drops to a relatively constant value once the average isolated H region size was larger than the critical size. In addition, it was noted that even though H evolves early in the annealing process, it was experimentally shown that MRO in the films were not significantly altered with the removal of most H in the film [14].

To summarise Mahan’s crystallisation model [14]: nucleation sites are the regions in dashed circles as shown in Figure 2.5, containing isolated H. The sizes of the nucleation sites relative to the theoretically calculated critical cluster size for nucleation determine the crystallisation kinetics [14]. If the nucleation sites are equal to or larger than the critical size, less time is required to build up clusters with critical size. The incubation time will be shorter and the nucleation sites crystallised to form nuclei more readily. Conversely, if the nucleation sites are smaller than the critical size, more time is required to build up clusters of critical size and a longer incubation time is observed [14].

For Mahan’s crystallisation model, some points are still open to debate as this model cannot completely explain the correlation between the a-Si:H structure, the nucleation behaviours and average grain sizes. Assuming each nucleation site yields one stable growth nucleus, this model suggests that larger nucleation sites will be closer to the critical cluster size for nucleation and hence should have shorter incubation times (and higher nucleation rates). This model then implies that faster SPC kinetics should be associated with larger grain sizes, and vice versa. This is however not always observed experimentally and in our work it will be shown in Chapters 4 and 5 that samples which crystallised the fastest usually end up with the smallest average grain sizes. Another important parameter not discussed by Mahan’s model is the density of nucleation sites which could have determined the average grain sizes in the poly-Si material. This issue
will be further discussed in Chapter 4. Nevertheless, the notion of the anisotropic nature of a-Si:H structure is still accepted due to ample experiment evidence presented in the literature. In this Thesis, we consider regions of higher ordering within the anisotropic a-Si:H material as nucleation sites and their number density as the nucleation site density.

### 2.4 Topics on poly-Si fabrication via SPC

The ideal a-Si:H structures for SPC poly-Si are not fully identified in the literature and hence optimal conditions for the fabrication of a suitable a-Si:H could not yet be recommended; unlike for µc-Si, where high deposition pressure, high power density and very high frequency (up to 100 MHz) PECVD deposition conditions are known to achieve material with a lower defect density and consequently resulting in better thin film solar cells [27-31]. The lack of such guidelines for the precursor a-Si:H material for SPC poly-Si is an indication that the SPC process is not yet well understood.

From Section 2.3 we learnt that MRO can be one key a-Si:H structural parameter. Zeman et al. [32] reported an improved MRO in a-Si:H by flowing H₂ together with the SiH₄ mixture during RF-PECVD (H₂ dilution). While improved MRO may be beneficial for a-Si:H based thin film solar cells, it may not be suitable as a precursor for SPC poly-Si thin film solar cells. For example, Mahan et al.[14] reported a better MRO for HWCVD deposited a-Si:H due to a higher degree of H clustering compared to RF-PECVD deposited a-Si:H. Average grain sizes for poly-Si derived from HWCVD deposited a-Si:H were reported to be 0.6 – 1.4 μm [33], while in the case of RF-PECVD at SERIS, average grain sizes were usually >1.5 μm. The smaller grain sizes from HWCVD suggest that higher MRO materials are associated with higher density of nucleation sites. For poly-Si thin films, grain sizes which are large enough to allow the formation of columnar grains were typically preferred and to achieve that, the grain sizes should be at least close to the film thickness of ~2 μm. A high MRO may not be recommended since...
the average grain size would be reduced and columnar grain growth would not be possible. Hence in the a-Si:H materials used in this work, little or no H\textsubscript{2} dilution of SiH\textsubscript{4} was used during deposition. Engineering low MRO a-Si:H materials is therefore identified as a topic of interest.

It was found that short range order (SRO, 1 – 3 Å) is related to the bond angle distortion from the ideal c-Si bond angle of 109.5° [34]. It has been reported that SRO has an effect on the grain size [35, 36] due to nucleation rate suppression. For the deposition conditions investigated in this work, the SRO for as-deposited a-Si:H was found to be invariant. However the effect of SRO should not be ignored as it is still not completely understood.

Other than the grain morphology, the recommended deposition conditions to allow poly-Si grain growth with reduced number of dislocations has not been well studied. While there are post-SPC treatments such as rapid thermal annealing (RTA) [37] that can annihilate point defects, line defects (dislocations) are more difficult to remove by thermal treatment especially with the temperature limitation due to the glass substrate. Hence it is best to minimise the dislocation incorporation during the SPC step. To improve the understanding and control over dislocations in poly-Si material, it is important to locate, identify and study the origin of the dislocations.

2.5 Overview of the Thesis

From Section 2.4, knowledge gaps were identified and the goal of this thesis is to gain more insights and to contribute to the understanding of SPC poly-Si material for applications in thin film solar cells.

The expanding thermal plasma (ETP) deposition technique will be explored in Chapter 4 of this thesis. This work is done in collaboration with the Eindhoven University of
Technology (TU/e). The characteristics of the ETP deposition technique are remote deposition, very high deposition rates and almost non-existent ion bombardment (<2 V) [38, 39]. Due to very distinct SPC kinetic behaviours for the different ETP samples, this work serves as a good demonstration for the empirical application of the apparent Avrami exponent in this Thesis.

Desired a-Si:H structures suitable as a precursor for SPC poly-Si are not fully identified due to the complicated nature of a-Si:H structure. So far MRO is identified as one possible key structural parameter, however, other than H₂ dilution, no other reports on MRO engineering were found for a-Si:H deposited by RF-PECVD. Chapter 5 of this thesis shows that MRO can be engineered by deposition pressure during RF-PECVD. This work suggest that the a-Si:H films should be deposited at lower pressures in order to obtain a lower MRO.

In Chapter 6, we utilised the electron backscatter diffraction (EBSD) as well as scanning transmission electron microscopy (STEM) to locate and study the dislocations in poly-Si material. The presence of geometrically necessary dislocations (GNDs) was found in grains > 3 µm. GNDs have not been formally identified in poly-Si material previously and it was suggested that GNDs can be reduced by limiting the grain size to <3 µm. GNDs are most likely associated to stress and plastic deformation during SPC.

Chapter 7 is a preliminary work which shows that the a-Si material is evolving as the SPC progresses. This chapter provides a new insight into the SPC process, which may be related to the stress within the Si film during SPC. The observations in this work are not yet well understood and further work will be required.
The chapters are written in a self-contained manner, with specific introduction and experimental sections relevant to each individual chapter. For convenience to the readers, some equations may be repeated.

References


Chapter 3 Experimental Section

The precursor amorphous silicon (a-Si:H) films for solid phase crystallisation (SPC) were fabricated by plasma enhanced chemical vapour deposition (PECVD) techniques, specifically, expanding thermal plasma (ETP) deposition and radio frequency parallel plate PECVD (RF-PECVD). For the study of a-Si:H properties, characterisation methods, such as ex-situ X-ray diffraction (XRD), Fourier Transform infrared spectroscopy, spectroscopic ellipsometry and Raman spectroscopy, were utilised. The SPC dynamics were monitored using in-situ XRD, while the polycrystalline silicon material structure was studied mainly using electron backscatter diffraction and scanning transmission electron microscopy. The key characterisation methods are discussed here, while the others will be briefly covered in the respective chapters.
3.1 Deposition methods

Two variants of plasma enhanced chemical vapour deposition (PECVD) were employed in this work to deposit hydrogenated amorphous silicon (a-Si:H) films, namely, the expanding thermal plasma (ETP) deposition technique and radio frequency parallel plate PECVD (RF-PECVD). The ETP of a-Si:H films were provided by Eindhoven University of Technology (TU/e) while the RF-PECVD depositions were done at the Solar Energy Research Institute of Singapore (SERIS).

3.1.1 The expanding thermal plasma deposition technique

The ETP deposition technique is a remote plasma technique [1], where the plasma generation and the substrate region are spatially separated (Figure 3.1), allowing independent optimisation of each region. Due to the remote nature of the plasma, ion bombardment is virtually non-existent (< 2 V). However, ion bombardment on the substrate during processing (i.e. deposition or etching) can be controlled via externally applied substrate biasing [2].

The plasma is generated by a direct current (DC) discharge in a non-depositing mixture of argon and hydrogen confined in a narrow channel of 2 – 4 mm diameter [3]. The plasma generation channel is maintained at typical pressures of 150 – 450 torr and the plasma leaves the channel through a nozzle and expands into the deposition chamber which is maintained at typical pressures of 0.075 – 0.225 torr. For deposition of a-Si:H, SiH₄ is mixed into the plasma just after the nozzle by an injection ring and chemically dissociates mainly by atomic hydrogen. For silicon nitride deposition, NH₃ is added to the deposition precursor gas mix in addition to SiH₄. High density of reactive species can be attained for this technique, allowing high processing rates.
3.1.2 Radio frequency parallel plate plasma enhanced chemical vapour deposition technique

The RF-PECVD technique, a direct plasma technique, is commonly used in the industry for deposition of a-Si:H thin films. An excitation frequency of 13.56 MHz is typically used to ionise precursor gases (such as SiH₄, B₂H₆ and PH₃) by electron impact ionisation to form a plasma. Since reactive species are formed in the plasma, the substrate can be maintained at a relatively low temperature compared to conventional CVD methods, which requires higher temperatures to thermally break down the precursor gases. Figure 3.2 shows the schematic of a typical RF-PECVD system setup, with a RF generator connected to the electrodes to initiate the plasma [4]. The system used in this research project is an asymmetrical system, with the substrate at the grounded electrode.
The grounded electrode is connected to the chamber wall, creating a condition where the area of the grounded electrode is larger than the powered electrode. Deposition rates for a-Si:H are typically 1 – 4 Å/s with significantly higher ion energy bombardment than the ETP technique.

![Figure 3.2. Schematic of a typical RF-PECVD system [4].](image)

Table 3-1 summarises the typical film growth and plasma properties for the ETP and PECVD technique.

<table>
<thead>
<tr>
<th>Property</th>
<th>ETP</th>
<th>RF-PECVD (13.56 MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate (nm/min)</td>
<td>Up to 4800 [1]</td>
<td>Up to 250 [5]</td>
</tr>
<tr>
<td>Ion energy (eV)</td>
<td>&lt; 2 (tunable) [1, 6]</td>
<td>200 – 1000 [7]</td>
</tr>
<tr>
<td>Electron temperature (eV)</td>
<td>0.2 – 0.3 [8]</td>
<td>1 – 5 [7]</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>0.07 – 0.4 [1]</td>
<td>0.01 – 1 [7]</td>
</tr>
</tbody>
</table>
3.2 Characterisation methods

In this section, the characterisation techniques that were used in this work will be discussed in detail. It is to be noted that in the examples given, the samples used may not be the same. For instance, the samples used in the examples for spectroscopic ellipsometry and Fourier Transform Infrared spectroscopy are different and should not be compared.

3.2.1 In-situ XRD

The SPC dynamics of the amorphous silicon (a-Si:H) thin film was studied by in-situ XRD (Panalytical X’pert Pro XRD, the Netherlands, equipped with Anton Paar HTK 1200N high temperature chamber). Figure 3.3 shows the setup of the in-situ XRD system. A copper target source of 1.54 Å was used and the high temperature chamber was maintained at a pressure of 10^{-4} to 10^{-5} mbar. The set temperatures used for SPC in the high temperature chamber were typically between 570 and 620 °C. The XRD scanning mode was lock-coupled and the Si (111) peak area centred at 2\( \theta = 28.5^\circ \) was used to monitor the phase change of the Si film from a-Si:H to polycrystalline silicon (poly-Si). Only one peak was required to monitor the phase change because it was shown that after SPC of a-Si:H, the grains in the poly-Si were randomly oriented (see Section 3.2.6). Table 3-2 summarises the expected XRD peak positions and their relative intensities.
Figure 3.3. Setup of the in-situ XRD system used in this work.

<table>
<thead>
<tr>
<th>Plane</th>
<th>2(\theta) (°)</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>28.5</td>
<td>100</td>
</tr>
<tr>
<td>(220)</td>
<td>47.5</td>
<td>54.9</td>
</tr>
<tr>
<td>(311)</td>
<td>56.4</td>
<td>29.7</td>
</tr>
<tr>
<td>(222)</td>
<td>59.1</td>
<td>0.1</td>
</tr>
<tr>
<td>(400)</td>
<td>69.4</td>
<td>6.9</td>
</tr>
<tr>
<td>(331)</td>
<td>76.7</td>
<td>9.4</td>
</tr>
<tr>
<td>(442)</td>
<td>88.5</td>
<td>11.4</td>
</tr>
</tbody>
</table>

Table 3-2. The expected XRD peaks for c-Si, 2\(\theta\) angles, and their relative intensities [11].

It is known that the integrated peak intensity of the XRD signal at a crystal peak scales linearly with the concentration of a component [12] and the XRD crystal fraction, \(f(t)\) is given by:

\[
f(t) \propto \frac{I_{c-Si}(t)}{I_{c-Si}(t_{sat})}
\]  

\(I_{c-Si}(t)\) is the intensity of the XRD peak at 2\(\theta = 28.5^\circ\) at time = \(t\), while \(I_{c-Si}(t_{sat})\) is the intensity of the XRD peak at time = \(t_{sat}\), where the peak intensity saturates and stops.
increasing. The crystal fraction can then be obtained by normalising $I_{c-Si}(t)$ with respect to $I_{c-Si}(t_{sat})$.

As an example, Figure 3.4 shows the evolution of the Si (111) peak as a function of time and the corresponding SPC dynamics. In the transformation profile, it was observed that there exists an initial period of apparent inactivity before the phase transformation proceeds. This period is known as the incubation period. Eventually the transformation profile saturates, which is an indication of complete transformation process, with crystal fraction of 1. The incubation period and the saturation at 100% crystallinity are indicated in Figure 3.4b.

![Figure 3.4](image)

**Figure 3.4.** (a) Evolution of the Si (111) XRD peak as a function of time. (b) The corresponding SPC dynamics showing the crystal fraction as a function of time. The error bar is based on the standard deviation of the data points at 100% crystallinity.

### 3.2.2 Ex-situ XRD

It is known that the first a-Si:H X-ray diffraction (XRD) scattering peak (centred at 2θ ~27.5°) has major contributions from the medium range order (MRO) [13, 14]. MRO is a term used to describe the structural ordering of a-Si:H on a length scale up to 5 nm. The
broader the full width half maximum (FWHM) of the first a-Si:H X-ray scattering peak, the lower the MRO [14-17]. A pseudo-Voigt function best describes the background scattering peak from the glass substrate while the a-Si:H scattering peak was described by a Pearson VII function following the work of Zeman et al. [17]. The XRD (Bruker D8 ADVANCE, Germany) 2θ scanning range was between 15° and 40°, with a step size of 0.05°. The X-ray source had a wavelength of 1.54 Å. Figure 3.5 shows the fitting of a-Si:H scattering peak centred around 27.5°.

![Figure 3.5](image)

**Figure 3.5.** Fitting of XRD peaks in order to extract the FWHM of diffraction peak from a-Si:H. The FWHM of the a-Si:H diffraction peak gives information on the medium range ordering of the a-Si:H film. A large FWHM indicates a reduced medium range order.
3.2.3 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum 400, USA) was utilised in the mid-IR range (400 – 4000 cm\(^{-1}\)) and the Near-IR range (2000 – 15700 cm\(^{-1}\)).

Mid-IR range

In the mid-IR range, the characteristic absorption of Si-H\(_x\) vibrations can be found. The characteristic absorptions and the vibration modes in a-Si:H are summarised in Table 3-3 [18]. The stretching modes at 1980 – 2030 cm\(^{-1}\) and 2060 – 2160 cm\(^{-1}\) are commonly referred to as the low stretching mode (LSM) and high stretching mode (HSM), respectively [19]. A microstructure factor, \(R^*\), is commonly defined as \(R^* = \frac{I_{\text{HSM}}}{I_{\text{LSM}} + I_{\text{HSM}}}\), where \(I_{\text{HSM}}\) and \(I_{\text{LSM}}\) correspond to the integrated absorption strength of the HSM and LSM, respectively [20].

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>590</td>
<td>SiH(_2) rocking mode</td>
</tr>
<tr>
<td>640</td>
<td>SiH(_3), SiH(_2), SiH wagging mode</td>
</tr>
<tr>
<td>850, 890</td>
<td>SiH(_2), SiH(_3) bending mode</td>
</tr>
<tr>
<td>1980 – 2160</td>
<td>SiH, SiH(_2) stretching mode</td>
</tr>
</tbody>
</table>

The samples in this project were mainly deposited on glass which is opaque to the mid-IR range and hence FTIR with the attenuated total reflection attachment (FTIR-ATR, MiRacle ATR, Pike technologies, USA) had to be employed as conventional transmission measurements were not possible. Figure 3.6 shows the typical FTIR spectrum of a-Si:H on glass in the mid-IR region via FTIR-ATR method.
A single reflection FTIR-ATR setup is shown schematically in Figure 3.7. A Ge crystal is part of the ATR setup and sample is in direct contact with the crystal. Pressure clamps were used to ensure good contact between the sample and the Ge crystal. In the ATR setup, the choice of the crystal and angle of incidence are crucial to ensure that the condition of total internal reflection is satisfied. The criterion is governed by the Snell's law:

\[ n_1 \sin \theta_1 = n_2 \sin \theta_2, \]  

(3.2)

where \( n_1 \) is the refractive index of Ge which is 4, \( \theta_1 \) the incident angle which is fixed at \( 45^\circ \), \( n_2 \) the refractive index of the sample and \( \theta_2 \) is the refracted angle. For total internal reflection to occur, \( \theta_2 \) has to be \( \geq 90^\circ \). Hence it can be calculated for total internal reflection to occur, \( n_2 \) has to be \( \leq 2.8 \). The IR refractive index of a-Si:H is typically \( \geq 3.4 \).
where the condition for total internal reflection criterion is not satisfied. From Eq. (3.2), it can be found that total internal reflection occurs at the SiNx layer instead which has an IR refractive index of ~2.1. Total internal reflection would then occur at the a-Si:H/SiNx interface as shown in Figure 3.7.

An evanescent wave is formed when total internal reflection occurs at the interface between two mediums as shown in Figure 3.7. Some of the radiation in the evanescent wave can be absorbed by the sample and the remaining radiation is reflected and returned to the detector.

The overall spectrum includes absorption from the IR radiation from the transmission through the a-Si:H films as well as the evanescent wave absorption from both the SiNx film and the glass substrate. The typical mid-IR absorption spectra in the LSM and HSM regions are shown in Figure 3.8. In this work, the SiNx thickness was kept as a constant and its absorption peak could be described by a single Gaussian peak fixed at 2169.6 cm$^{-1}$ as indicated in Figure 3.8. The peak position at 2169.6 cm$^{-1}$ was verified to be due to SiNx from the measurements of reference SiNx coated glass samples. This absorption peak is most likely associated with the H$_2$Si-N$_2$ stretching mode since it is the closest to 2175 cm$^{-1}$ (see Table 3-4). For more information on the ATR technique, readers are referred to the work by Fujiwara and co-workers [21] and the references therein.
Figure 3.7. Schematic illustration of the interaction of IR light in our sample configuration. Due to the relative high refractive index of the a-Si:H film the condition for total internal reflection at the Ge/a-Si:H is not met and, consequently, the IR beam is partly transmitted. Total internal reflection only takes place at the a-Si:H/SiNx interface.

Table 3-4. The vibration modes and the associated frequencies of SiN\(_x\) (or more precisely, a-Si\(_{x}N_{y}H_{z}\)) in the IR range [18].

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>845 – 870</td>
<td>SiN stretching mode</td>
</tr>
<tr>
<td>1175</td>
<td>NH(_2) NH(_2) wagging and rocking mode</td>
</tr>
<tr>
<td>2005</td>
<td>HSi-Si(_3) stretching mode</td>
</tr>
<tr>
<td>2082</td>
<td>HSi-NSi(_2) stretching mode</td>
</tr>
<tr>
<td>2140</td>
<td>HSi-N(_2)Si, H(_2)Si-NSi stretching mode</td>
</tr>
<tr>
<td>2175</td>
<td>H(_2)Si-N(_2) stretching mode</td>
</tr>
<tr>
<td>2220</td>
<td>HSi-N(_2) stretching mode</td>
</tr>
<tr>
<td>3445</td>
<td>NH(_2) stretching mode</td>
</tr>
</tbody>
</table>
Near-IR range

FTIR in the near-IR range of 1500 – 1950 nm was used in the transmission mode to obtain the refractive indices of the silicon films. In this wavelength region, both the silicon film and the SiNx film are transparent (or only weakly absorbing) and their respective refractive indices can be modeled using a Cauchy dispersion relation and the extinction coefficient can be taken as zero.

The Cauchy relationship is typically given by [22]

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}. \]  

(1)

\( A, B \) and \( C \) are empirical parameters used for fitting.

The refractive index of the glass substrate was taken to be constant in this wavelength range following the method published by Swanepoel et al.[23]. Reference samples of the
bare glass and SiN$_x$ coated glass were measured separately to obtain their refractive indices. Figure 3.9a shows a typical transmission spectrum in the near-IR range of between 1500 nm and 1950 nm and Figure 3.9b shows the corresponding refractive index of a-Si:H from fitting of the transmittance spectrum. It is to be noted that while the wavelength range of 300 to 1200 nm is of interest for the optical response of a solar cell in this case, however, the refractive index obtained in the Near-IR range is useful because the refractive index in the Near-IR region has been found to have an empirical correlation with the mass density of the film [24, 25].

![Figure 3.9](image)

Figure 3.9. (a) Typical transmittance spectrum in the 1500 – 1950 nm wavelength range of a glass/SiN/a-Si:H sample. The glass refractive index was found to be a constant in this wavelength range and the SiN$_x$ and a-Si:H optical functions were modeled by a Cauchy dispersion relation. The open circles represent the experimental data and the solid line represents the fit obtained using the Swanepoel model [26]. (b) The corresponding refractive index of a-Si:H obtained from the fitting in (a).

3.2.4 Spectroscopic ellipsometry

Spectroscopic ellipsometry (Sopra, GES5E, France) measures the change in polarisation of light after its interaction with a sample. The change in polarisation is
expressed by two parameters: amplitude ratio (ψ) and phase difference (Δ). These parameters are affected by the thickness, dielectric function and surface roughness of a material and from a model based analysis of ψ and Δ, the thicknesses and dielectric functions of a-Si:H and SiNx can be extracted. The Tauc-Lorentz model [27] is typically used to model a-Si:H and SiNx films and the surface roughness can be modeled by an effective medium approach assuming 50% void and 50% a-Si:H material [28]. Figure 3.10 shows a typical measurement data of a glass/SiN/a-Si:H sample structure which is commonly expressed as tan ψ and cos Δ. Figure 3.11 shows the corresponding refractive index of a-Si:H extracted from the measurement. Measurements are typically done between 1.5 eV and 4.9 eV in this work.
Figure 3.10. Example of measured (a) $\tan \psi$ and (b) $\cos \Delta$ for Glass/SiN/a-Si:H sample structure.

Figure 3.11. The corresponding complex refractive index of the a-Si:H obtained from the analysis of $\tan \psi$ and $\cos \Delta$ from Figure 3.10. The thickness of the film as determined from the model based analysis of the spectroscopic ellipsometry data is indicated in the figure as well.
3.2.5 Raman spectroscopy

Raman spectroscopy (Renishaw, inVia, UK) was used to determine the short range structural ordering (SRO) of a-Si:H. An argon light source with a centre wavelength of 514 nm with a variable spot sizes from 1 to 20 µm was used. During measurement, the power was kept below 50 mW to prevent crystallisation of the sample. The Raman vibration modes and associated peak positions are summarised in Table 3-5. For a-Si:H, the TO mode FWHM is an indication of the bond angle deviation ($\Delta \theta$) from the standard c-Si bond angle of 109.5° [29-32]. $\Delta \theta$ can be calculated by [29]:

$$\Gamma = 15 + 6 \Delta \theta,$$

(3.3)

where $\Gamma$ is the FWHM of the Raman TO peak for a-Si:H.

The characteristic c-Si peak is centred at ~521 cm$^{-1}$. Figure 3.12 shows a Raman spectrum of a partially crystallised a-Si:H demonstrating the characteristic peaks mentioned in Table 3-5.

<table>
<thead>
<tr>
<th>Raman vibration modes</th>
<th>Peak position (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transverse Acoustic (TA) mode</td>
<td>150</td>
</tr>
<tr>
<td>Longitudinal Acoustic (LA) mode</td>
<td>310</td>
</tr>
<tr>
<td>Longitudinal Optical (LO) mode</td>
<td>410</td>
</tr>
<tr>
<td>Transverse Optical (TO) mode</td>
<td>480</td>
</tr>
</tbody>
</table>
Figure 3.12. An example of Raman spectroscopy measurement taken from a partially crystallised a-Si:H sample showing the c-Si peak centred at ~521 cm$^{-1}$ and the a-Si:H characteristic peaks, TO, LO, TA, LA modes.

All the peaks can be described with a Gaussian profile and the peak positions of TA, LA, LO modes are fixed while the TO and the c-Si peak positions and intensities were released as fitting parameters during analysis.

3.2.6 Electron backscatter diffraction

Electron backscatter diffraction (EBSD, Bruker CrystAlign 200, Germany) is a technique capable of acquiring micro-structural orientation information. Electrons are ideal for our application on poly-Si thin films as the probing size is smaller than the typical grain sizes (in the order of 1 µm). The EBSD detector is an attachment to the scanning electron microscope (SEM, Carl Zeiss AURIGA, Germany). This technique is attractive as it allows a relatively fast mapping of the region of interest with statistically useful crystallographic information. For more detailed information on this technique, readers can refer to a review paper by Humphreys [33].
Figure 3.13. Photograph of the EBSD setup within the SEM chamber. The sample is tilted 70° and electron is incident on the sample from the top. The diffracted electrons are then picked up by the EBSD detector.

For the EBSD analysis, the sample was tilted in the SEM chamber such that an angle of 20° is made between the incident electron beam and the sample surface as shown in Figure 3.13. The electrons scatter and form an interaction volume within the poly-Si material and some of the electrons are scattered such that Bragg’s law is satisfied. These electrons are diffracted and the Kikuchi diffraction patterns formed are captured by the EBSD detector. A schematic for the formation of Kikuchi patterns is shown in Figure 3.14a and an example of the Kikuchi pattern is shown in Figure 3.14b.

The source of electron scattering can considered to be between lattice planes and hence a pair of parallel lines Kikuchi band is formed for every family of planes. The Kikuchi patterns are analysed real time by comparison with a database of diffraction patterns to a given crystallographic orientation. For example, Figure 3.15a shows the diffracted electrons from a crystal forming a Kikuchi pattern on the phosphor screen of the EBSD detector. Figure 3.15b shows a simulated Kikuchi pattern (with inputs of tilt angle and sample distance from detector) while Figure 3.15c shows the fitting of the pattern. Each
Kikuchi band has a distinct width which corresponds to inter-planar spacing and hence a crystallographic plane. Intersection of bands in the Kikuchi pattern corresponds to a zone axis where the crystallographic planes involved (identified by the Kikuchi bands that are intersecting) are parallel to the zone axis direction. The Kikuchi pattern contains all angular relationships of a crystal (inter-zonal and inter-planar angles) and hence also the crystal symmetry. By identifying the zone axes and the bands together with their respective angular relationships in the Kikuchi patterns, the crystallographic orientation of the volume from which the Kikuchi pattern is produced can be identified. Our EBSD system can capture the diffraction patterns and index at a speed up to 32 pixels s$^{-1}$ or higher depending on the diffraction signal strength. Higher speeds are desired to minimise the effects of drifting during the mapping. The typical electron acceleration voltages are between 10 to 20 kV with an electron beam current within the range of 10 nA.

![A schematic of Kikuchi pattern formation.](image)

Figure 3.14. A schematic of Kikuchi pattern formation.
There are two sets of coordinates used to specify an orientation – a specimen coordinate system \((C_s)\) and a crystal coordinate system \((C_c)\). \(C_s\) consists of axes X, Y and Z while \(C_c\) consists of axes [100], [010] and [001]. **Figure 3.16** shows the two coordinate systems, where:

- \(\alpha_1, \beta_1\) and \(\gamma_1\) are the rotation of the [100] axis onto X, Y and Z sample axes, respectively.
- \(\alpha_2, \beta_2\) and \(\gamma_2\) are the rotation of the [010] axis onto X, Y and Z sample axes, respectively.
- \(\alpha_3, \beta_3\) and \(\gamma_3\) are the rotation of the [001] axis onto X, Y and Z sample axes, respectively.
An orientation matrix \( (g) \) can then be defined as

\[
C_c = g \cdot C_s,
\]

where \( g \) embodies the rotation of the specimen coordinates onto the crystal coordinates.

\[
g = \begin{pmatrix}
\cos \alpha_1 & \cos \beta_1 & \cos \gamma_1 \\
\cos \alpha_2 & \cos \beta_2 & \cos \gamma_2 \\
\cos \alpha_3 & \cos \beta_3 & \cos \gamma_3
\end{pmatrix} = \begin{pmatrix}
g_{11} & g_{12} & g_{13} \\
g_{21} & g_{22} & g_{23} \\
g_{31} & g_{32} & g_{33}
\end{pmatrix}.
\]

\[\text{Figure 3.17}\] shows an example of an EBSD orientation map, where each colour represents a specific crystallographic orientation of the grains. All poly-Si samples studied in this Thesis exhibited a random grain orientation. More discussion can be found in Chapter 6 where the EBSD technique will be extended to study defects in poly-Si by measuring the small rotation changes within each grain.
3.2.7 High angle annular dark field scanning transmission electron microscopy

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM, Tecnai G2 F20 X-Twin transmission electron microscope) was used to image dislocations in the poly-Si material. Figure 3.18 shows the schematic setup of the HAADF-STEM imaging. An incident convergent beam scans the sample surface and the electrons that transmit straight through are collected by the bright field detector. The HAADF detector is a ring around the bright field detector and positioned close to the sample to collect electrons which are scattered at higher angles ($\theta > 50$ mrad).

Dislocation contrast features appear in HAADF-STEM images due to the Bloch-wave scattering effect. The Bloch-wave scattering effect will not be discussed here and the description of this effect can be found elsewhere [34]. Figure 3.19 shows an example of a HAADF-STEM image of a poly-Si thin film sample. Dislocations appear as bright lines in the HAADF-STEM images.
Figure 3.18. Schematic of the HAADF-STEM setup.

Figure 3.19. Example of a HAADF-STEM image of a poly-Si thin film specimen.
The samples were prepared by first mechanical polishing followed by ion milling to further thin down the sample. The acceleration voltage used for HAADF-STEM viewing was 200 kV.

### 3.3 Summary

Table 3-6 below summarises the different characterisation techniques and the corresponding information that we can obtain.

<table>
<thead>
<tr>
<th>Characterisation technique</th>
<th>Information obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-situ XRD</td>
<td>SPC dynamics and crystallinity</td>
</tr>
<tr>
<td>XRD</td>
<td>Medium range order of a-Si:H, crystal orientations</td>
</tr>
<tr>
<td>FTIR Mid-IR</td>
<td>a-Si structural information and hydrogen content</td>
</tr>
<tr>
<td>FTIR Near-IR</td>
<td>Near IR refractive index</td>
</tr>
<tr>
<td>Spectroscopic ellipsometry</td>
<td>Thickness and optical function</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>Short range order of a-Si and crystallinity</td>
</tr>
<tr>
<td>EBSD</td>
<td>Grain size, grain morphology and defect characterisation</td>
</tr>
<tr>
<td>HAADF-STEM</td>
<td>Dislocation imaging</td>
</tr>
</tbody>
</table>

### References


Chapter 4 Kinetic Study of Solid Phase Crystallisation of Expanding Thermal Plasma Deposited Amorphous Silicon

*In-situ* X-ray diffraction is used to study the dynamics of the solid phase crystallisation (SPC) of hydrogenated amorphous silicon (a-Si:H) films deposited by expanding thermal plasma technique (ETP). Results from parallel plate radio frequency plasma enhanced chemical vapour deposition (RF-PECVD) deposited a-Si:H are also included as a comparison. The apparent Avrami exponent $n$ was used to empirically group the a-Si:H materials. It was observed that a-Si:H which crystallised with $n > 4$ showed larger columnar grains as well as a more robust SPC process. The a-Si:H samples which crystallised with $n < 4$ had much smaller grains as well as SPC dynamics which are not repeatable. In this chapter, relationships among the apparent Avrami exponent $n$, the SPC process stability and the subsequent grain structure were demonstrated. Under certain conditions, the ETP films exhibited columnar grain structure with the indications of good grain quality, suggesting that these films are suitable to be further developed into solar cell devices. It was found that the average grain sizes of the poly-Si were not solely dependent on the SPC dynamics, suggesting that the nucleation site density is important as well. It is suggested that a-Si:H films deposited by ETP have a higher nucleation site density compared to RF-PECVD a-Si:H. While the interpretation of $n$ values is ambiguous, this chapter shows that $n$ is still useful if used empirically to group the a-Si:H materials with different SPC behaviours.
4.1 Introduction

The polycrystalline silicon (poly-Si) active layer is typically fabricated by first depositing a layer of amorphous silicon (a-Si:H) via radio frequency parallel plate plasma enhanced chemical vapour deposition (RF-PECVD), followed by the solid phase crystallisation (SPC) process, where the a-Si:H film crystallises in a furnace to form poly-Si at temperatures around 600 °C [1]. The typical deposition rates of the RF-PECVD process are 45 nm/min or lower [2] and this process step is considered as the major bottleneck for this technology. In an attempt for higher deposition rates, other deposition techniques such as e-beam evaporation deposition [3], sputtering [4], hot-wire chemical vapor deposition (HWCVD) [5, 6] have been considered. A high-rate RF-PECVD process with deposition rates up to 250 nm/min was reported with no degradation in solar cell device performance in the resulting SPC poly-Si [7]. However, the deposition rate of a-Si:H is still a major challenge for the fabrication process.

The expanding thermal plasma (ETP) is another interesting candidate for the high-rate deposition of a-Si:H films. The ETP technique was developed at the Eindhoven University of Technology (TU/e) and has already been successfully commercialised for the deposition of silicon nitride (SiNx) and silicon oxide (SiOx) anti-reflective coatings on silicon wafer solar cells [8]. For a-Si:H, deposition rates up to 4.8 µm/min have been demonstrated, however, a deposition rate of 480 nm/min was found to be most suitable for device grade a-Si:H layers [9]. It should be noted that device grade a-Si:H may not be required for the SPC process, hence, deposition rates higher than 480 nm/min can be explored for this application. It has been shown [10] that poly-Si with a grain size up to 1 µm could be obtained by SPC of ETP-grown a-Si:H films that were deposited at 480 nm/min. Some initial kinetic studies on the SPC of a-Si:H deposited by ETP were conducted [11] but a more detailed study is still required.
In this chapter, we will study the SPC dynamics of ETP deposited a-Si:H films using in-situ X-ray diffraction (XRD) as the main diagnostic tool. It will be shown that a-Si:H materials can be grouped into two types based on their $n$ values.

### 4.2 Experimental

Undoped a-Si:H films with SiN$_x$ interfaces were deposited by the ETP technique on glass substrates (Corning 7059) resulting in a sample structure as shown in **Figure 4.1**. Details of the ETP technique are given elsewhere [9] and in Chapter 3. The deposition conditions used for the a-Si:H deposition are summarised in Table 4-1. Samples deposited at a substrate temperature of 200 and 400 °C were labelled 200ETP and 400ETP, respectively. For ETP deposition, three substrates (2.5 cm × 2.5 cm each) were mounted on a substrate holder and deposited using one single ETP plasma source. After the deposition, each sample was sectioned into smaller pieces of 1 cm × 1 cm and subjected to the SPC process at temperatures in the range from 590 to 620 °C.

![Figure 4.1](image-url)  
**Figure 4.1.** Schematic structure of the samples used to study the SPC dynamics of ETP deposited a-Si:H films.
Table 4-1. Deposition parameters for ETP deposited a-Si:H.

<table>
<thead>
<tr>
<th>Sample</th>
<th>200ETP</th>
<th>400ETP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar flow (sccs)</td>
<td>25</td>
<td>55</td>
</tr>
<tr>
<td>SiH₄ flow (sccs)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>H₂ flow (sccs)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>200</td>
<td>400</td>
</tr>
<tr>
<td>Deposition rate (nm/min)</td>
<td>150</td>
<td>420</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>~860</td>
<td>~970</td>
</tr>
</tbody>
</table>

**Figure 4.2** shows the sample structure of the RF-PECVD sample used for comparison with the ETP samples in this work. Undoped a-Si:H films were deposited on SiNₓ coated borosilicate glass (Schott Borofloat 33) substrates. The deposition conditions are summarised in Table 4-2. For the RF-PECVD deposition, 30 cm × 40 cm borosilicate glass substrates were used and subsequently sectioned into smaller pieces of 1 cm × 1 cm for further analyses.

**Figure 4.2.** Schematic structure of the samples used to study the SPC dynamics of RF-PECVD deposited a-Si:H films.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature (°C)</td>
<td>360</td>
</tr>
<tr>
<td>Power density (mW/cm²)</td>
<td>33</td>
</tr>
<tr>
<td>SiH₄ flow (sccm)</td>
<td>40</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>0.6</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>~1000</td>
</tr>
</tbody>
</table>

The temperature ramping profile used for the SPC process is shown in Figure 4.3. This temperature profile features a hydrogen out-diffusion step at 450 °C to prevent film damage from hydrogen evolution at higher temperatures later on in the SPC process. Furthermore, the maximum temperature ramping rate was capped at 20 °C/min to prevent film damage from thermal shock.

![Temperature-time profile](image)

**Figure 4.3.** Temperature-time profile used for the SPC process. The samples were held at a temperature of 450 °C for 60 min to drive out hydrogen from the films. Subsequently, the samples were heated to their respective SPC temperatures in 45 min. The samples were held at the SPC temperatures for 10 h or more.
The characterisation techniques utilised in this work are *in-situ* XRD, Raman spectroscopy, electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). Details on these techniques can be found in Chapter 3.

### 4.3 Results

#### 4.3.1 SPC dynamics study of ETP a-Si:H with *in-situ* XRD

Figure 4.4 shows the fraction of crystallinity as a function of time for 200ETP a-Si:H films derived from *in-situ* XRD. The films were annealed at four different temperatures between 590 and 620 °C. From Figure 4.4, we can learn that all films exhibited a non-zero incubation time during SPC. Higher SPC temperatures resulted in shorter incubation times as well as higher rates of crystallisation.

![Figure 4.4. Fraction of crystallinity as a function of time determined for the SPC of 200ETP a-Si:H films. The symbol sizes were adjusted to represent the measurement error (±0.02), which was taken to be the standard deviation of the measurement at crystallinity fraction of 1.](image)

On the other hand, 400ETP a-Si:H films behaved inconsistently as shown in Figure 4.5, where the sample annealed at 600 °C unexpectedly completed the SPC process ahead
of the sample annealed at 610 °C. In addition, the sample annealed at 600 °C also did not exhibit any incubation time prior to crystallisation. While only three samples are shown in Figure 4.5, a total of five samples were tested within the range of 590 to 620 °C and all samples showed little or no incubation time with no detectable trends observed.

![Graph showing crystal fraction as a function of time for 400ETP a-Si:H films annealed at various temperatures. SPC behaviours were found to be inconsistent for these samples.]

**Figure 4.5.** Crystal fraction as a function of time for 400ETP a-Si:H films annealed at various temperatures. SPC behaviours were found to be inconsistent for these samples.

### 4.3.2 SPC dynamics study of RF-PECVD a-Si:H with *in-situ* XRD

**Figure 4.6** shows the fraction of crystallinity as a function of time for RF-PECVD a-Si:H films derived from *in-situ* XRD. The films were annealed at five different temperatures between 580 and 620 °C. The SPC behaviours were as expected, with the lowest temperature taking the longest time to complete the SPC process.
Figure 4.6. Crystal fraction as a function of time for RF-PECVD a-Si:H films annealed at various temperatures. The error bar represents the measurement error (± 0.04) which was taken to be the standard deviation of the measurements at crystal fraction of 1. All data points have the same measurement error.

4.3.3 On the apparent Avrami exponents

Extraction of the apparent Avrami exponent \( n \) is covered in Section 2.2 of this Thesis and as discussed, interpretation of the \( n \) values will be ambiguous and should not be attempted. The apparent Avrami exponent will be used in an empirical manner in this Thesis.

The \( n \) values for the 200ETP, 400ETP and RF-PECVD films were extracted and shown in Figure 4.7, Figure 4.8 and Figure 4.9, respectively. 200ETP and RF-PECVD films had \( n \) values \( \sim 7 \) while most of the 400ETP films had \( n \) values < 4. The SPC process for the 400ETP is unstable and no trend was observed.
Figure 4.7. Apparent Avrami exponents $n$ for 200ETP samples at various temperatures. Samples A and B are repeats of the experiment at the same temperature, i.e. 590A and 590B are repeats of the SPC experiment at 590 °C.

Figure 4.8. Apparent Avrami exponents $n$ for 400ETP samples at various temperatures. Sample 610A and 610B are repeats of the SPC experiment at 610 °C. Results suggest that the SPC process for 400ETP samples is unstable.
4.3.4 Medium range order in a-Si:H

As mentioned in Section 2.3, it is known in the literature that the medium range order (MRO) can affect the SPC dynamics. The SPC dynamics at 600 °C for the three samples are shown in Figure 4.10 and it can be observed that the incubation time for 200ETP > RF-PECVD > 400ETP sample.
Information on the MRO can be obtained from *ex-situ* XRD measurements (Section 3.2.2) on as-deposited a-Si:H films, where a larger XRD full width half maximum (FWHM) represents a lower MRO. Figure 4.11 shows a good correlation between the MRO and the incubation time during SPC, where a lower MRO is associated with a longer incubation time. The XRD data for the ETP samples were measured at TU/e [12] while the XRD data for the RF-PECVD sample is from Chapter 5. The apparent Avrami exponent and the average grain size of each sample after SPC is indicated under each data point. The apparent Avrami exponent also shows some correlation with the MRO, where lower MRO is associated with higher \( n \) values. However, the average grain sizes did not show any correlation with the MRO and the incubation time.

Figure 4.10. SPC kinetics of 200ETP, 400ETP and RF-PECVD samples at 600 °C. It can be observed that 400ETP have little or no incubation time while 200ETP had the longest incubation time.
Figure 4.11. The XRD FWHM as a function of incubation time. The larger the FWHM, the lower the MRO of the a-Si:H. A good correlation is found among the MRO, the incubation time and the apparent Avrami exponent \((n)\), while no correlation is found for the average grain sizes for the samples after SPC. XRD FWHM data for the ETP samples were measured at TU/e [12] and the error bars were assumed to be the same as the RF-PECVD sample measured.

4.3.5 Post-SPC analysis

Figure 4.12a and Figure 4.12b show the cross section TEM dark field images of typical ETP poly-Si films with \(n < 4\) and \(n > 4\), respectively. The films with \(n < 4\) featured randomly distributed grains in the bulk of the film with grain sizes estimated to be 100 nm or less. For films with \(n > 4\), most of the grains surveyed showed large columnar grains spanning the entire film thickness.

Figure 4.12c shows the cross section TEM dark field image of a typical RF-PECVD poly-Si film with \(n > 4\). Most grains surveyed demonstrated large columnar grains spanning the entire film thickness.
Figure 4.12(a). Cross section TEM dark field image of a 400ETP sample showing the presence of small silicon crystals with a size 100 nm or less. Inset: corresponding diffraction pattern of the image, suggesting presence of small and randomly distributed silicon crystals.

Figure 4.12(b). Cross section TEM dark field image of a 200ETP sample. Large columnar grains spanning the entire film thickness were formed. Inset: corresponding diffraction pattern of the image with characteristics of large grains.
In addition to the characteristic silicon 521 cm\(^{-1}\) Raman peak, films with \(n < 4\) also featured an extra Raman peak at 510 cm\(^{-1}\) as shown in Figure 4.13, which was found to be associated to the existence of small defective silicon crystals [13].
Figure 4.14 shows the normalised XRD intensity for the post-crystallised 200ETP, 400ETP and RF-PECVD poly-Si samples annealed at 600 °C. The XRD FWHM for the RF-PECVD, 200ETP and 400ETP samples are (0.155 ± 0.005)°, (0.20 ± 0.03)° and (0.38 ± 0.05)°, respectively. In the order of increasing XRD FWHM: RF-PECVD < 200ETP < 400ETP. The broader XRD peaks for films with \( n < 4 \) films suggest the presence of small crystallites and non-uniform strain [14], which is in agreement with TEM and Raman spectroscopy measurement.

![Graph showing XRD intensity vs. 2θ](image)

Figure 4.14. The normalised XRD peaks were fitted by a Pearson VII function. The XRD FWHM of the peaks extracted are (0.155 ± 0.005)°, (0.20 ± 0.03)° and (0.38 ± 0.05)° for the RF-PECVD, 200ETP and 400ETP poly-Si samples, respectively. The RF-PECVD poly-Si demonstrated the narrowest XRD peak while the 400ETP sample demonstrated the widest peak.

The average grain sizes of 200ETP and RF-PECVD poly-Si films were determined from EBSD measurements and Figure 4.15 shows the average grain sizes as a function of SPC temperature. The grain size of the 400ETP films was difficult to be determined as the grain sizes were close to the detection limit of our EBSD system. TEM images suggest the grain sizes of 400ETP films to be \( \leq 100 \) nm. It can be seen that the RF-
PECVD samples yielded significantly larger average grain sizes compared to 200ETP samples at > 1.5 µm and < 1 µm, respectively. For RF-PECVD samples, the average grain sizes were found to drop relatively quickly from 590 to 610°C (~2.5 to ~2 µm). The average grain sizes appear to be invariant at ~2 µm from 610 to 620°C and this could be explained by the similarity in SPC kinetics between these two temperatures (see Figure 4.6). The average grain sizes for 200ETP on the other hand were found to decrease more gradually from 590 to 620°C.

![Figure 4.15. Average grain sizes of 200ETP and RF-PECVD poly-Si samples as a function of SPC temperatures. The dotted lines serve as a guide to the eye.](image)

### 4.4 Discussion

Clear differences were observed between the a-Si:H materials which crystallised with $n < 4$ and $n > 4$. Hence in this Thesis, we group the a-Si:H into two groups: $n < 4$ a-Si:H material and $n > 4$ a-Si:H material. The $n < 4$ a-Si:H materials typically crystallise after a short or no incubation time and form very small grains. The $n < 4$ a-Si:H material also exhibited an unpredictable and non-repeatable SPC process, which means that the SPC process for $n < 4$ a-Si:H is not easily controlled and thus not desirable for manufacturing.
On the other hand, \( n > 4 \) a-Si:H material always crystallise with an incubation time. Large columnar grains were also commonly observed. Formation of columnar grains could be the result of stress and/or thermal gradients in the direction perpendicular to the substrate leading to preferential growth in the perpendicular direction. An equiaxial columnar grain could also be the result of a growing grain without impingements from any nucleation events and allowed to span the entire film thickness.

The observation of little or no incubation periods for \( n < 4 \) samples indicates that nucleation sites in these samples crystallise to form nuclei more readily, while the observation of incubation periods in \( n > 4 \) samples indicates that nucleation sites in these samples crystallise to form nuclei less readily. Results suggest that the lower MRO in the a-Si:H material is correlated to nucleation sites which form nuclei less readily and vice versa. In other words, the MRO could be a measure of the degree of ordering in the nucleation sites, which in turn is an indication of how readily the nucleation sites crystallise to form nuclei.

As shown in Section 4.3.4, the average grain sizes of the poly-Si did not show any correlation with the incubation time and MRO. Hence it is becoming clear that the average grain size of the poly-Si is not completely determined by the SPC dynamics. 200ETP a-Si:H films have a longer incubation period and a slower SPC rate compared to RF-PECVD a-Si:H films, however, against the intuition, the average grain sizes of RF-PECVD is more than two times those of the 200ETP samples (see Figure 4.15). We propose that the density of the nucleation sites affect the average grain size in the poly-Si material after SPC and this seems to be related to the deposition techniques. Results suggest that ETP a-Si:H has a higher nucleation site density compared to RF-PECVD a-Si:H, hence resulting in consistently smaller grains for ETP derived poly-Si material.
TEM showed that poly-Si films obtained from 200ETP and RF-PECVD films yielded mainly large columnar grains, extending from the bottom to the top of the film. This macrostructure is essential in photovoltaic applications as minority carriers travel perpendicular to the substrate without barriers from grain boundaries.

4.5 Conclusions

In-situ XRD was used to study the SPC dynamics of a-Si:H films deposited by the ETP technique and comparisons were made with the SPC dynamics of RF-PECVD deposited a-Si:H. From the SPC dynamics, the apparent Avrami exponent $n$ was extracted and used empirically to group the a-Si:H material. It was observed that $n < 4$ a-Si:H materials resulted in very small grained ($\leq 100$ nm) poly-Si material and the SPC process is not robust, which is not desirable for manufacturing. On the other hand, $n > 4$ materials resulted in large columnar grains and the SPC process is more robust and repeatable. A good correlation was found between MRO and the incubation time; however, no correlation was found between the average grain sizes of poly-Si and these parameters. It was proposed that the MRO measured in the a-Si:H films could be a measure of ordering in the nucleation sites. The average grain size in the poly-Si material is not solely related to the SPC dynamics but also associated with the nucleation site density. The nucleation site density of ETP samples can be suggested to be higher than that of the RF-PECVD sample since the average grain sizes of ETP samples are consistently smaller than that of the RF-PECVD samples regardless of the SPC dynamics.
Acknowledgments

We like to thank Dr. Kashish Sharma from TU/e for supplying the ETP samples. We also thank Prof. Stefan Adams (National University of Singapore, Department of Materials Science and Engineering) for the fruitful discussions as well.

References


Publications related to this chapter:


Conference proceedings related to this chapter:

In recent years, medium range ordering (MRO) in amorphous silicon (a-Si:H) is identified as one key structural parameter in controlling its solid phase crystallisation (SPC) behaviour. In this work, it was found that the pressure during a-Si:H film deposition can control the MRO in a-Si:H thin films. A threshold behaviour during SPC was observed as a function of the deposition pressure of the a-Si:H film and a good correlation between the SPC behaviour and the MRO in a-Si:H was found. Higher MRO in a-Si:H led to faster SPC rates and smaller grain sizes. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and ultraviolet reflectance measurements indicate that films with higher MRO yielded polycrystalline silicon (poly-Si) grains which were more defective and non-columnar in morphology. Results suggest that a-Si:H material with lower MRO were preferred as a precursor for SPC, which forms better quality poly-Si thin film materials. It was proposed that ion bombardment seems to play a role in altering the a-Si:H properties.
5.1 Introduction

Polycrystalline silicon (poly-Si) thin film solar cells have the potential to achieving energy conversion efficiencies of >13% at low cost with a relatively simple device structure. Poly-Si thin film solar cell modules feature a robust monolithic design with the use of non-toxic and stable materials, such as Si which are abundant in supply [1]. Poly-Si is typically fabricated by the solid phase crystallisation (SPC) of amorphous silicon (a-Si:H), where the a-Si:H film crystallises at temperatures above 550 °C [2]. The highest efficiency reported up to now for SPC based poly-Si thin film solar cell is 10.5% for a 20 cell mini-module (94 cm²) [3, 4]. The a-Si:H film is typically deposited by radio frequency parallel plate plasma enhanced chemical vapour deposition (RF-PECVD), but other techniques, such as e-beam deposition [5], hot wire chemical vapour deposition [6] and expanding thermal plasma deposition [7-11] have also been used.

The quality of the poly-Si material is a key concern in poly-Si thin film solar cells and recent trends point towards intra-grain defects as the main limitation in solar cell performance rather than the grain size [12]. The structural properties of a-Si:H desired for SPC poly-Si thin film solar cells still have to be defined. Consequently, the deposition conditions required for the optimum a-Si:H material for SPC poly-Si (average grain size of 1 – 2 µm) are not yet established, unlike for microcrystalline silicon (average grain size of < 100 nm) where a high deposition pressure, high plasma power and very high frequency conditions are known to result in low defect density material [13-17]. The common deposition parameters which may affect a-Si:H materials include substrate temperature, power, pressure, frequency and deposition precursor gases (such as SiH₄, Si₂H₆, SiHCl₃ etc.) [2, 12, 18]. It is acknowledged that RF-PECVD deposition has a huge parameter space and different deposition systems could result in different film properties even with similar deposition conditions. Hence this work focuses on the structural
properties of the silicon films, aiming to enhance the understanding of the type of a-Si:H materials preferred, which could result in poly-Si materials which are less defective and suitable for solar cell applications. With better understanding of the a-Si:H material properties required coupled with the knowledge of plasma physics and chemistry, good control of the SPC poly-Si technology can eventually be realised.

Sanyo reported that a-Si:H with low short range order (SRO, up to 3 Å length scale) would result in larger average grain sizes after SPC due to nucleation rate suppression [2, 18]. However, the associated intra-grain quality of the poly-Si materials obtained was not reported. While the medium range ordering (MRO, up to 5 nm length scale) in a-Si:H has been studied for many years, earlier works mainly focused on applications for a-Si:H thin film solar cells, where a-Si:H film with higher MRO seems to be preferred [19-25]. MRO improvement was observed by introducing H₂ gas into the deposition chamber (H₂ dilution) with the other precursor gases during the deposition [19, 21, 25]. In recent years, the MRO of the a-Si:H material for SPC application has received growing interest from the community and the common consensus is that lower MRO materials lead to longer incubation times and lower rates of crystallisation [11, 26]. However, in the literature, there are no reports on the relation between the MRO and the subsequent poly-Si intra-grain quality. In addition, the resulting grain morphology is not well studied for RF-PECVD deposited SPC poly-Si films. In this work, the reduction of MRO in a-Si:H was shown to be possible with the lowering of deposition pressure. Relationship among the MRO, SPC dynamics and the intra-grain quality of the resulting poly-Si film are reported.
5.2 Experimental

Intrinsic hydrogenated amorphous silicon (a-Si:H) films were deposited on silicon nitride (SiNₓ, ~ 75 nm) coated borosilicate glass substrates (30 cm x 40 cm) with a thickness of 3.3 mm. The a-Si:H layer was deposited using RF-PECVD (MV Systems, USA) at a substrate temperature of 360°C and using a SiH₄ flow of 40 sccm and a RF plasma power density of 33 mW/cm². The deposition pressure was varied from 0.2 to 1.0 Torr and the deposition time was adjusted such that the a-Si:H films were of approximate equal thickness of ~1 µm.

The characteristic infrared absorption of Si-Hₓ vibrations in a-Si:H films on glass were probed using attenuated total reflection Fourier transform infrared (ATR-FTIR, Perkin Elmer Spectrum 400, USA, with Pike Technologies MIRacle ATR attachment) spectroscopy. The hydrogen content cannot be easily extracted based on the ATR-FTIR method since the absorbance intensities are affected by the quality of the contact between the a-Si:H film and the germanium crystal in the ATR setup (See section 3.2.3). Nevertheless, the relative peak intensity can still be used in the analyses. The stretching modes at 1980 – 2030 cm⁻¹ and 2060 – 2160 cm⁻¹ are typically referred to as the low stretching mode (LSM) and high stretching mode (HSM), respectively [27]. The microstructure factor \( R^* \) is defined as \( R^* = \frac{l_{\text{HSM}}}{l_{\text{LSM}} + l_{\text{HSM}}} \), where \( l_{\text{HSM}} \) and \( l_{\text{LSM}} \) corresponds to the integrated absorption strength of the HSM and LSM modes, respectively [27]. The LSM can be attributed to Si-H bonds situated in either mono-vacancies or di-vacancies [28]. However, the origin of the HSM is still debated in the literature. Some authors have reported a good correlation between the HSM and the 890 cm⁻¹ bending mode [29-31]. Since the 890 cm⁻¹ peak is typically assigned to the Si-H₂ bending mode, Kageyama et al. [32] recently assigned the HSM to the SiH₂ stretching mode. In addition, the nano-void density of a-Si:H films was found to increase linearly.
with the HSM integrated absorbance, implying that these Si-H$_2$ bonds are residing in the inner surfaces of nano-voids, hence, HSM can be interpreted as Si-H$_2$ in nano-voids [32, 33].

Spectroscopic ellipsometry (J.A. Woollam Co., VASE Ellipsometer, USA) was used to obtain the thickness as well as the dielectric function of a-Si:H films from the 0.55 to 4.5 eV photon energy range. The dielectric function of the a-Si:H films was modelled using the Tauc-Lorentz model [34]. Surface roughness was modelled by an effective medium approach assuming 50% void and 50% a-Si:H material [35].

It has been well accepted that first a-Si:H X-ray diffraction (XRD) scattering peak (centred at 2$\theta$ $\sim$27.5°) has major contributions from the MRO [19-25]. The broader the full width half maximum (FWHM) of the first a-Si:H scattering peak, the lower the MRO [19-26]. A pseudo-Voigt function best describes the background scattering peak from the glass substrate while a-Si:H scattering peak was described by a Pearson VII function following the work of Zeman et al. [25] The XRD (Bruker D8 ADVANCE, Germany) 2$\theta$ scanning range was between 15° and 40°, at a step size of 0.05°. The X-ray source has a wavelength of 1.54 Å.

The SPC dynamics were studied by high temperature in-situ XRD (Panalytical X’pert Pro XRD, the Netherlands, equipped with Anton Paar HTK1200N high temperature chamber, Austria). The X-ray source wavelength used was 1.54 Å and the chamber was maintained at a pressure of $<10^{-4}$ Pa. The XRD scanning mode was lock-coupled and the phase transformation from amorphous state to polycrystalline state was monitored based on the Si (111) peak centred at 2$\theta$ = 28.5° [7]. Each sample was sectioned into smaller pieces of 10 mm x 10 mm and subjected to the SPC process in the XRD oven at a substrate temperature of 570 °C. The temperature-time profile used for the SPC
process is shown in Figure 5.1. In addition, the apparent Avrami exponent $n$ was extracted from the SPC dynamics. Extraction of $n$ is discussed in Section 2.2 of this thesis.

![Temperature-time profile used during the SPC process. After 180 minutes, the temperature is held at 570 °C for 15 hours.](image)

Based on comparison between Raman spectroscopy, optical transmission microscopy and transmission electron microscopy (TEM), Straub et al. [36] showed that the crystal quality of the poly-Si can be determined from the reflectance peaks centred at around 275 and 360 nm. These two peaks are related to the direct optical transitions at critical points in crystalline silicon which broaden and decrease in amplitude with an increasing defect density in the crystalline silicon material [37]. This method was adopted in this work to analyse the crystal quality of the poly-Si obtained. From the reflectance measurements (PerkinElmer LAMBDA 950 UV/VIS spectrophotometer, USA), a quality factor, $Q$ can be defined as [36]:

$$Q = \frac{R_{275} + R_{360}}{2}$$
\[ Q = \frac{1}{2} \left[ \left( \frac{R_{e1}}{R_{e1-C-Si}} \right) + \left( \frac{R_{e2}}{R_{e2-C-Si}} \right) \right], \quad (5.1) \]

where \( R_{e1} \) and \( R_{e2} \) are the heights of the reflectance peaks of the samples centred around 275 nm and 360 nm, respectively. \( R_{e1-C-Si} \) and \( R_{e2-C-Si} \) are the corresponding peak heights of a reference crystalline silicon wafer.

To further support the poly-Si grain quality investigation, scanning transmission electron microscopy (STEM, Tecnai G² F20 X-Twin, FEI, USA) imaging was conducted on poly-Si material for dislocation imaging using a high angle annular dark field (HAADF) detector [38, 39]. Samples were prepared by mechanical polishing followed by further thinning by Ar ion milling. Acceleration voltage used during imaging was 200 kV.

An electron backscatter diffraction (EBSD, Bruker QUANTAX CrystAlign, Germany) detector on a scanning electron microscope (SEM, Carl Zeiss Auriga, Germany) was used to extract a grain orientation map in order to extract the average grain size. The electron acceleration voltage in the SEM was set between 10 and 20 kV with an electron beam current up to 11 nA.

\section*{5.3 Results}

\subsection*{5.3.1 Amorphous silicon material properties}

\textbf{Figure 5.2} shows the deposition rate of the a-Si:H films as a function of the deposition pressure. The deposition rate of samples at 0.2 and 0.4 Torr had a similar deposition rate of \(~11\) nm/min while the sample deposited at 0.6 Torr had a deposition rate of \(~15\) nm/min. The deposition rate further increased to \(~20\) and \(~22\) nm/min for samples deposited at 0.8 and 1.0 Torr, respectively. It can be observed that deposition rates gradually increase with pressure.
Information on the MRO could be extracted with ex-situ XRD measurements of the a-Si:H films [23, 25]. As mentioned in Section 3.2.2, the larger the FWHM of the a-Si:H first scattering peak (centred at ~27.5°), the lower the MRO. Based on the XRD FWHM, the samples can be grouped into two types, namely Type A and Type B as shown in Figure 5.3. Type A consist of samples deposited at 0.2 – 0.6 Torr while Type B samples consist of samples deposited at 0.8 – 1.0 Torr. A threshold behaviour was observed, with Type A samples having lower MRO compared to Type B samples.
Figure 5.3. FWHM of the first a-Si:H scattering peak as a function of the deposition pressure of the a-Si:H film. The samples can be grouped into two groups, namely Type A and Type B as indicated in the figure.

Figure 5.4a shows $R^*$ as a function of deposition pressure. It can be observed that sample deposited at 1.0 Torr had the highest $R^*$ value, suggesting that a larger fraction of hydrogen is bonded in the nano-voids. $R^*$ decreases with decreasing deposition pressure, reaching a minimum at 0.6 Torr. $R^*$ then increases slightly as the deposition pressure decreases from 0.6 to 0.2 Torr.
Figure 5.4. (a) $R^*$, (b) apparent Avrami exponent, $n$, (c) average grain size, (d) UV reflectance quality factor $Q$, as a function of deposition pressure.

5.3.2 SPC kinetics

Figure 5.5 shows the SPC dynamics derived from *in-situ* XRD measurements. A threshold behaviour is observed – Type A and Type B samples clearly demonstrated different SPC dynamics, with Type B samples showing significantly shorter incubation times and/or faster crystallisation rates. In addition, Type A samples exhibited similar SPC kinetics, suggesting a robust SPC process.

Figure 5.4b shows the apparent Avrami exponents $n$ as a function of deposition pressure. It can be observed that Type A samples have similar $n$ values of $> 7$. While Type B samples have lower $n$ values of $< 6$. 
5.3.3 Post-SPC analysis

Figure 5.4c shows the average grain size of poly-Si obtained from a-Si:H deposited at different pressures. Type A samples form poly-Si material with similar grain sizes of ~2.3 µm after SPC while Type B samples form poly-Si with significantly smaller grain sizes after SPC. The Type B sample deposited at 1.0 Torr formed poly-Si with the smallest average grains of less than 1 µm.

Figure 5.4d shows the UV reflectance quality factor ($Q$) of the poly-Si materials obtained after the SPC of a-Si:H deposited at different pressures. It can be observed that the highest poly-Si film quality was formed by a-Si:H deposited at the lowest pressure of 0.2 Torr while the lowest poly-Si film quality was formed by a-Si:H deposited at the highest pressure of 1.0 Torr. In general, Type A samples have a better $Q$ than Type B samples.
Multiple grains from a Type A sample (0.6 Torr) and a Type B sample (1.0 Torr) were sampled using HAADF-STEM and selected images are shown in Figure 5.6. Type A and Type B samples are shown in Figure 5.6a–c and Figure 5.6d–f, respectively. The grains aligned for dislocation imaging are indicated by arrows and labelled “poly-Si”. It was found that the Type A poly-Si film had predominantly columnar grains extending throughout the film thickness, while for the Type B poly-Si film, columnar grains were rarely found. The grains found in the Type B poly-Si film are typically irregular in shape and occasionally extends throughout the entire film thickness. Small grains in the range of ~200 nm (Figure 5.6f) were also commonly observed in the Type B film than in the Type A film. From the HAADF-STEM images, it can be observed that the Type A films have a higher density of dislocations compared to the Type B films.

Figure 5.6. (a) – (c): HAADF-STEM images of a Type A sample (0.6 Torr). (d) – (f): HAADF-STEM of a Type B sample (1.0 Torr). Arrows labelled “poly-Si” indicate grains which are aligned for dislocation imaging. Columnar grains were more commonly observed for Type A samples than Type B samples. Type A samples on average also have grains with lower dislocation densities compared to Type B samples.
5.4 Discussion

The MRO showed good correlation with the SPC behaviour, with the Type A samples showing distinctively lower MRO compared to Type B samples. It is also interesting to note that all Type A films have almost the same SPC dynamics, demonstrating a robust SPC process. It was observed that Type A samples had higher $n$ values compared to that of Type B samples, with Type B samples approaching the value of 4. While the interpretation of $n$ values are challenging, it has been observed in Chapter 4 that lower $n$ values are associated with small and defective poly-Si grains which are not desired.

Both UV reflectance and HAADF-STEM indicate that Type A films yielded better quality poly-Si grains than Type B films. HAADF-STEM images show that Type A poly-Si have predominantly columnar grains extending throughout the film thickness, indicating that growing grains were allowed to grow without impingement from any nucleation of new nuclei. On the other hand, for Type B samples, while continuous grains extending throughout the film thickness can be observed, these grains were usually irregularly shaped rather than columnar in shape. The grain morphology of Type B poly-Si suggests that the existing grains which were growing during the SPC process were frequently impeded by nucleation of new grains. This observation suggests that nucleation rates are higher in Type B samples than in Type A samples.

Changes in plasma properties for different deposition pressures may include ion bombardment energy, gas phase polymerisation as well as shift in plasma discharge regime. The energy of the ions bombarding the growing a-Si:H film is known to be reduced with increasing deposition pressure [13, 16, 40, 41]. The reduction in ion energy at higher pressures could be explained by the multiple collisions experienced by the ions while traversing through the plasma sheath [17, 42]. These collisions result in the ions losing energy prior to reaching the substrate. As shown by Smets et al., ion energies of $\leq$
50 eV are sufficient to cause drastic reduction in nano-void density from nano-void collapse, while ion energies of $\geq$ 150 eV can cause slight increase in nano-void density due to ion induced sputtering [43]. Indications of both effects seem to be present in Figure 4a, where nano-void collapse causes $R^*$ to drop drastically from 1.0 Torr to 0.6 Torr. From 0.6 Torr and below, $R^*$ increases slightly, which could suggest the onset of ion induced sputtering. Results suggest that a threshold ion bombardment energy (in the region of 150 eV) may be required to reduce the MRO in a-Si:H to form Type A samples.

While gas phase polymerisation [44-47] may be involved with increasing deposition pressure, this effect cannot explain the higher MRO observed at higher pressures. Gas phase polymerisation occurs when mean free path of primary reaction products are reduced due to higher pressure and undergo secondary reaction with additional SiH$_4$ molecules. This leads to the formation of polysilane (SiH$_x$)$_y$ ($y > 1$) molecules which contribute to film growth at the substrate [44-47]. Film growth contribution from polysilanes is typically associated with higher nano-void content related to lower surface diffusion mobility as well as steric hindrance from these larger radicals during film incorporation [45]. Both lower surface mobility and steric hindrance will likely lead to increase in structural disorder, which contradicts the results of Figure 5.3 where a better structural order is observed at higher deposition pressures.

An increase in deposition pressure may also cause a shift in plasma discharge regime (from $\alpha$ to $\gamma$) [48, 49], where regime shifts were characterised by sudden increase in deposition rates. While Figure 5.2 shows an increase in deposition rate with the increase in pressure, further investigations are required to verify if a shift in plasma discharge regime has occurred.
A detailed study of the changes in plasma physics and chemistry is called for to determine the root cause of changes in a-Si:H structural properties. The changes in $R^*$ as a function of pressure suggest that ion bombardment may play a role in altering the a-Si:H properties. While the deposition pressure was isolated as a variable in this work, other parameters should be explored as well in the future.

5.5 Conclusions

Films with a lower medium range order (MRO) exhibited higher values of the apparent Avrami exponent ($n$), larger grain size and demonstrate a robust SPC process while films with higher MRO have lower values of $n$ and smaller grain size. The shorter incubation times, the smaller grain sizes and irregular grain morphologies suggest that films with higher MRO have higher nucleation rates compared to films with lower MRO. HAADF-STEM and UV reflectance results suggest that lower MRO a-Si:H films yielded poly-Si grains which are less defective. MRO in a-Si:H films can be modified by adjusting deposition pressure and it was proposed that with pressure changes in the deposition chamber, ion bombardment may play a role in altering the a-Si:H structural properties.

References


**Publications related to this chapter:**

Electron backscatter diffraction (EBSD) was used to characterise dislocations in poly-Si thin films that were obtained from solid phase crystallisation of amorphous silicon. EBSD allows the precise measurement of the spatially resolved crystal orientation and thus can detect small rotations in the material thereby providing information on the lattice curvature. Since geometrically necessary dislocations (GNDs) are associated with lattice curvatures, their presence can thus indirectly be detected by EBSD. In this work, the presence of GNDs in poly-Si was detected, suggesting that plastic deformation occurs during the SPC process. The elevated temperatures during SPC allow the GNDs to rearrange into arrays, forming low angle grain boundaries. We found that GNDs start forming in poly-Si grains with sizes > ~3 µm. GNDs are extra defects in addition to the existing statistically stored dislocations that form during grain growth and hence more care needs to be taken to minimise the formation of GNDs.
6.1 Introduction

Polycrystalline silicon (poly-Si) thin films have potential for low cost applications in photovoltaics. This technology features a monolithic module design and uses silicon as the active material, which is stable, abundant and non-toxic. For poly-Si thin film solar cell fabricated by the solid phase crystallisation (SPC) method, a record efficiency of 10.4% for a 20 cell mini-module (94 cm²) is already demonstrated [1, 2]. Fabrication of poly-Si typically involves the deposition of the precursor amorphous silicon (a-Si:H) by radio frequency parallel plate plasma enhanced chemical vapour deposition (RF-PECVD) followed by the SPC step, where the a-Si:H film is crystallised at temperatures of above 550°C. Other deposition techniques, such as e-beam deposition [3], hot wire chemical vapour deposition [4, 5] and expanding thermal plasma deposition [6-9], are being investigated as well.

Recent advances in the understanding of the poly-Si based solar cell point towards intra-grain defects being the limiting factor in the solar cell device performance [10]. While defects at grain boundaries also degrade the solar cell device performance, it has been shown that these defects can be effectively passivated by a hydrogenation process [3]. Defects are undesirable in photovoltaic devices and a high level of defects in poly-Si thin film material is an indication that this technology is not fully understood and controlled. Intra-grain defects can manifest themselves in the form of point defects, intra-grain boundaries or dislocations. Σ3 grain boundaries are the dominant low energy intra-grain boundaries which form readily during Si crystal growth. Due to the crystallographic continuity at Σ3 grain boundaries, they are originally electrically inactive. However Chen et al. [11, 12] showed that regions around Σ3 boundaries in multi-crystalline Si wafers can be activated by gettering of Fe at high impurity levels. The more effective the gettering ability of the grain boundary, the more readily it can be activated. It was found
that random grain boundaries are the strongest in gettering ability while $\Sigma 3$ boundaries have the weakest gettering ability. Recently, van Gestel et al. [13] showed using electron beam induced current (EBIC) that for poly-Si, regions around $\Sigma 3$ boundaries are electrically active as well. It was noted that in this case, the poly-Si materials were formed by the aluminium induced crystallisation (AIC) method and the $\Sigma 3$ boundaries could potentially have been activated by Al impurities. Hence impurity control is important for poly-Si as well. Since it is generally accepted that dislocations are the dominant performance limiting defect for poly-Si solar cells, this will be the focus of the remainder of the Chapter. To improve understanding and control over the poly-Si thin film solar cell technology, it is essential to delineate, identify and study the origin of the dislocations present in the poly-Si thin films. Dislocations are difficult to remove from the poly-Si films and it is thus desirable to minimise dislocation incorporation during the SPC process. Dislocation can be grouped into two types, namely statistically stored dislocations (SSDs) and geometrically necessary dislocation (GNDs) [14]. Dislocations in poly-Si can be studied experimentally by a number of methods, such as EBIC, transmission electron microscopy (TEM) and scanning tunneling electron microscopy (STEM), just to name a few [15]. Secco etching [16], though very useful in the case of c-Si wafers for the detection of dislocations, is found to be less applicable for poly-Si thin films due to the high dislocation densities that are typically found in these films (in the order of $10^{10}$ cm$^{-2}$). On the other hand, EBIC is only suitable for detecting dislocations in large-grained poly-Si films as can be formed by the AIC process [13] or by direct epitaxial growth [17]. Fortunately TEM and STEM can be effectively used to characterise dislocations in small-grain poly-Si films [13, 15, 18, 19]. Finally, electron backscatter diffraction (EBSD) can be utilised to obtain crystal orientation maps from which inter-grain and intra-grain boundaries can easily be detected [13, 20, 21]. In this Chapter, it will be shown that EBSD can be used to visualise misorientations in poly-Si thin films
which are strong indications of the presence of GNDs. EBSD can be used to detect small lattice rotations, which provides information on the lattice curvature of the material. GNDs are accumulation of dislocations of the same sign and closely related to lattice curvature and hence readily detected by EBSD. While on the other hand, SSDs are formed by random growth defects and are not associated to curvature in the lattice and therefore cannot be detected by EBSD [22-24].

In addition we have used high angle annular dark field STEM (HAADF-STEM) to reveal dislocations within the poly-Si material which should include both SSDs and GNDs. We show that under certain process conditions (not far from our typical processing conditions), there are strong indications that GNDs are present in our SPC poly-Si films. GNDs are considered additional defects besides SSDs and should be minimised. This can be done with better understanding of GNDs.

6.2 Experimental

Deposition of both the a-Si:H and SiNx films were carried out by RF-PECVD cluster tool (MVSystems Inc., USA). During the deposition of intrinsic a-Si:H, a substrate temperature of 360 °C, power density of 33 mW/cm² and SiH₄ flow of 40 sccm with pressure of 0.6 Torr was used; while for n⁺ a-Si:H, conditions were the same, except a SiH₄ flow of 12 sccm and 2 sccm of PH₃ (2% PH₃ diluted in H₂) was used.

The a-Si:H films (thickness ~1 µm) were deposited on silicon nitride (SiNx, thickness ~75 nm) coated borosilicate glass (3.3 mm, 30 cm × 40 cm). SiNx acts as a barrier to impurity diffusion from the glass substrate as well as an anti-reflective coating. SPC of a stacked layer with different doping types and concentrations has been used in the fabrication of poly-Si thin film PV devices [25]. To understand the effect of stacking different doped layers, an n⁺ layer is added on top of an undoped layer to study the effects on SPC. Two
types of samples were used: undoped a-Si:H/SiNx/glass and $n^+$ a-Si:H/undoped a-Si:H/SiNx/glass. In this chapter, the first sample will be referred to as the a-Si:H($i$) sample and the second sample will be referred to as the a-Si:H($n^+$)/a-Si:H($i$) sample, while their post-SPC counterparts will be referred to as poly-Si($i$) sample and poly-Si($n^+$)/poly-Si($i$) sample, respectively.

The samples underwent a SPC process in a nitrogen purged furnace (Nabertherm, N120/65HAC, Germany) at 600 °C. The temperature-time profile is as follows: 1) 25 °C to 300 °C in 30 minutes, 2) 300 °C to 400 °C in 30 minutes, 3) hold at 450 °C for 1 hour, 4) 450 °C to 600 °C in 1 hour, 5) hold at 600 °C for 15 hours. After the SPC process, the oven is slowly cooled from 600 to 350 °C in approximately 4.5 hours. The oven door is then left ajar at 350 °C and allowed to cool to 80 °C in approximately one hour before the sample was removed.

The electrically active doping concentration in the $n^+$ layer was found to be $2 \times 10^{20}$ cm$^{-3}$ from electrochemical capacitance voltage (ECV, CVP21 ECV Profiler, WEP Control, Germany) measurements. The poly-Si films studied were locally exposed to 0.1 M of ammonium bifluoride, forming an electrolyte-semiconductor Schottky contact. As the poly-Si material was etched by the electrolyte, capacitance-voltage (C-V) measurements were taken at various depths. Analysis of the C-V measurements allows the active doping concentration profile to be extracted. More details on this technique may be found elsewhere [26-29].

EBSD (Bruker QUANTAX CrystAlign, Germany) was used to extract the grain orientation map of the poly-Si material obtained via SPC. The electron acceleration voltage was between 10 and 20 kV, with an electron beam current up to 11 nA. Step sizes in the grain orientation map are between 0.12 and 0.13 μm.
6.3 Geometrically necessary dislocations and lattice curvature

During plastic deformation, GNDs are formed to support the geometric change within a material. Due to the increase in dislocation density, the elastic strain energy stored in the material increases. Some stored energy can be released when the atoms are mobile at \( T > -0.3 \, T_m \) (corresponding to \( T > -424 \, ^\circ\text{C} \) in Si) and the GNDs can rearrange themselves into an array with equal spacing, forming a low angle grain boundary (LAGB) [30].

A symmetric pure tilt boundary shown schematically in Figure 6.1 is a simple case of the LAGB. This allows us to understand the relation between GNDs and the lattice curvature. Regions 1 and 2 are two sections of a grain separated by the LAGB. The distance \( dx \) is the distance over which a rotation (\( \theta_p \)) between the two regions is formed due to the GNDs. \( \theta \) is the small angle of rotation associated with one dislocation. In this case, the axis of rotation points out of the plane of the paper. Depending on the axis of rotation, the LAGBs can be classified into pure tilt boundaries, pure twist boundaries or a mix of both [30]. The nature of the LAGB cannot be easily determined due to the high uncertainty of the axis of rotation for small rotation angles in EBSD measurements [31].
Figure 6.1. Schematic of an array of GNDs, forming a low angle grain boundary which separates two regions within a grain. An accumulation of dislocations leads to a rotation of $\theta_T$ between the two regions of the grain.

The spacing between each dislocation is $D$ and $b$ is the Burgers vector. It can be deduced from Figure 6.1 that

$$\frac{b}{2D} = \sin \frac{\theta}{2} \quad (6.1)$$

and for small angles,

$$\frac{b}{D} \approx \theta. \quad (6.2)$$

For $n$ number of dislocations,

$$\frac{nb}{D} \approx \theta_T \quad (6.3)$$
where $\theta_T$ is the orientation difference between the two regions of crystals across the LAGB. Typical values of $\theta_T$ are $\leq \sim 5^\circ$ [30].

Figure 6.1 shows the formation of a lattice curvature across $dx$ with the inclusion of GNDs in the material. Lattice curvature is given by [32]:

$$\kappa = \frac{d\theta_T}{dx}. \quad (6.4)$$

Even though the axis of rotation is not well defined via EBSD, LAGB can still be identified in EBSD based on their characteristics: $\theta_T \leq \sim 5^\circ$ and highly localised orientation changes associated with the presence of an array of GNDs. Orientation changes can be represented by misorientation, which will be described in the next section.

### 6.4 Misorientation maps

From EBSD measurements, an orientation matrix $g$ can be obtained for every pixel, given by:

$$g = \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}. \quad (6.5)$$

The transformation matrix between two pixels ($g_1$ and $g_2$) is known as the misorientation ($M$), which is given by:

$$g_2 = Mg_1. \quad (6.6)$$

The misorientation angle of rotation ($\theta_M$) is given by [33]:

$$\theta_M = \cos^{-1}[(M_{11} + M_{22} + M_{33} - 1)/2]. \quad (6.7)$$
From the misorientation angle, misorientation maps can be derived. In this work, two types of misorientation maps were utilised, namely, grain average misorientation (GAM) map and the kernel average misorientation (KAM) map [23]. The difference between these two maps is how the reference orientation matrix \( g_1 \) is defined. For the GAM map, the reference orientation matrix is the average orientation matrix for a particular grain. For the KAM map, the reference orientation matrix is the average of a cluster of eight pixels surrounding the pixel of interest at the centre.

GAM maps allow the visualisation of misorientation gradients within the material by measuring the accumulated orientation changes relative to the average orientation within the grain. Hence the existence of misorientation gradients in GAM maps is a representation of plastic deformation in the material [23]. For measurement of elastic deformation, precise measurements of the lattice parameters are required, which is beyond the capability of our standard EBSD technique [23] and hence not observed. It is noted though Wilkinson et al. [22] managed to extract elastic strain information by careful examination of the zone axes shifts in the Kikuchi diffraction patterns. KAM maps on the other hand delineate the local misorientations, representing the spatial distribution of GND arrays [34].

While EBSD may not be sensitive enough to pick up individual GNDs, arrays of GNDs may invoke enough local orientation changes to be detected. GAM maps should contain information of all GNDs present in the material since it represents the plastic deformation in the material, while KAM maps only provide information on the location of GND arrays.
6.5 Results and discussion

6.5.1 The poly-Si (i) sample

Figure 6.2 shows the HAADF-STEM image for the poly-Si(i) sample. Multiple grains were surveyed and it was found that the grains were mostly columnar. Figure 6.3a shows the GAM map of the poly-Si(i) sample and a straight path is marked in solid white line in the inset. A misorientation profile along this path is plotted as shown in Figure 6.3b. The starting point is in the middle of the grain and end point is towards the edge of the grain. The starting point is taken as the reference pixel in this plot. Based on measurements of a single crystalline silicon wafer, the misorientation noise of the measurement was found to be ~1°. As shown in Figure 6.3b, a misorientation up to 2° was measured. Due to the relatively small misorientation angles, the signal to noise ratio was found to be low. Nevertheless, GAM map shows indication that misorientation gradients are present in some of the grains, suggesting the presence of GNDs. No indications of dislocation arrays were detected in the KAM map for this sample and hence results are not shown.

Figure 6.2. Cross-section HAADF-STEM micrograph of a grain in the poly-Si(i) sample.
Figure 6.3. (a) GAM map of the poly-Si sample. Inset: enlarged view of boxed region showing the path where the grain average misorientation profile was taken. (b) Misorientation along the path indicated in inset of Figure 6.3. The misorientation for every point was measured with respect to the first point. Even though the signal to noise ratio is low, this result still indicates the presence of misorientation gradient. The gradient in this misorientation profile suggests the presence of plastic deformation and hence the presence of GNDs.

The GAM map suggests that GNDs were likely to be located near the grain edges, however, the cross sectional HAADF-STEM image in Figure 6.2 shows that dislocations
also exist in the centre portion of the grain. Since SSDs do not contribute to lattice curvature and are not detected by EBSD, the dislocations observed in Figure 6.2 should contain a mix of both SSDs and GNDs. Results from Figure 6.2 and Figure 6.3 suggest SSDs dominate in this single layer sample.

6.5.2 The poly-Si\((n^+)/(i)\) sample

The average plan view grain size of the poly-Si\((n^+)/(i)\) sample is \(~7 \, \mu m\), with grain sizes up to \(16 \, \mu m\). Figure 6.4 shows the GAM map of the poly-Si\((n^+)/(i)\) sample, with extensive regions containing misorientation gradients (and hence plastic deformation) compared to the poly-Si\((i)\) sample in Figure 6.3.

![Figure 6.4](image)

Figure 6.4. (a) GAM map of the poly-Si\((n^+)/(i)\) sample. Fine white lines are the \(\Sigma 3\) boundaries while black lines are random grain boundaries. (b) The enlarged view of boxed region showing the path where a misorientation profile was taken. The misorientation profile is shown in Figure 6.5a. (c) KAM map of the boxed region. Two streaks of localised misorientation were observed. Fine white lines represent \(\Sigma 3\) boundaries while the thick white line represents the path where a misorientation profile is taken. The misorientation profiles are shown in Figure 6.5b and Figure 6.5c. (d) PQ map of the selected region. Two dark streaks of poor diffraction quality were observed and coincide with the localised misorientation in (c). Red lines represent \(\Sigma 3\) boundaries.
A red box in Figure 6.4a shows a region of interest that was chosen for a more detailed study. Figure 6.4b shows the enlarged view of the region of interest from the GAM map and a straight path is indicated. In Figure 6.5a, the misorientation profile is shown following the straight path defined in Figure 6.4b. The misorientation of each point is with reference to the first point. A misorientation gradient was observed along this path, suggesting the presence of GNDs in the region. The misorientation was found to increase up to $5^\circ$, which is twice that of the poly-Si(1) sample.

The KAM map was utilised to delineate regions of local misorientation, which is known to assist in visualising the spatial distribution of GNDs [22]. In the region of interest, the KAM map in Figure 6.4c revealed two streaks of local misorientation gradient, with a straight path indicated in white. Following the straight path, Figure 6.5b shows the misorientation profile with the misorientation taken relative to the first point. It can be observed that relative rotation of $\sim 5^\circ$ obtained across the two streaks of localised misorientation. Figure 6.5c follows the same path as well, with the misorientation of every point taken relative to the previous point. A local misorientation gradient of up to $\sim 5^\circ$ was observed.

Figure 6.4d shows the pattern quality (PQ) map from EBSD of the selected region. The PQ map is based on the contrast between the Kikuchi band edge and the background signal. Darker pixels represent a poorer contrast and indicate a poor crystal quality [23]. The two streaks from Figure 6.4c coincide perfectly with the two dark streaks of reduced diffraction quality in the PQ map. This suggests that the two streaks in Figure 6.4c are associated with defective regions in the grain.
Figure 6.5. (a) Misorientation profile along the path from the centre to the edge of the grain in Figure 6.4b. The misorientation is taken relative to the first point. A gradient in misorientation indicates the presence of plastic deformation and hence GNDs. (b) Misorientation profile along the path as indicated in Figure 6.4c. The misorientation at each point is taken relative to the first point. A misorientation of $\sim 5^\circ$ was observed across the streaks. (c) Misorientation profile along the path as indicated in Figure 6.4c. The misorientation at each point is taken relative to the previous point. The two regions of high local misorientations correspond to the two streaks as shown in Figure 6.4c and Figure 6.4d. The high localised misorientations in the two regions correspond to LAGB and their
locations are indicated with dash lines.

Figure 6.6a and Figure 6.6b shows cross sectional HAADF-STEM images of the poly-Si(n+)/poly-Si(i) sample. Several grains were sampled and it was observed that columnar grains were less frequently found compared to the poly-Si(i) samples. In addition, the distribution of dislocations in poly-Si(n+)/poly-Si(i) samples was clearly more anisotropic compared to the poly-Si(i) samples. Some grains exhibited features resembling dislocation cells as shown in Figure 6.6a. Dislocation cells are typically associated with plastic deformation and GNDs in the material [30], further supporting that plastic deformation had occurred during SPC. Figure 6.6b shows an anisotropic distribution of dislocation density, where higher densities of dislocations were observed near to the grain edge. These excess dislocations could be GNDs.
Figure 6.6. (a) Observation of dislocation cells in the stacked poly-Si thin film sample. Dislocation cells are typically associated with plastic deformation and GNDs, further suggesting that plastic deformation has occurred during SPC. (b) This micrograph clearly shows the anisotropic distribution of dislocations in the poly-Si material, which may be attributed to the presence of GNDs.

Since KAM maps revealed the existence of arrays of GNDs and it has been confirmed that $\theta_T \leq \sim 5^\circ$ across the arrays of GNDs, the two streaks of local misorientation in Figure 6.4c were identified as LAGBs [30]. During SPC, the temperature was $\sim 600 \, ^\circ C$ and rearrangement of GNDs into LAGBs can be expected. It is to be noted that while arrays of GNDs can be visualised in KAM maps; EBSD is not sensitive enough to detect isolated GNDs which may also be present in the poly-Si material. However, GAM maps represent plastic deformation and therefore should contain information of all GNDs present. To investigate the origin of GNDs in the grains, partially crystallised poly-Si($n^+$)/poly-Si($i$) samples were examined as well.

6.5.3 The partially crystallised poly-Si($n^+$)/poly-Si($i$) sample

Figure 6.7 shows the GAM map of a partially crystallised poly-Si($n^+$)/poly-Si($i$) sample. The black regions represent the amorphous phase while the coloured regions represent
the crystalline phase. For the partially crystallised samples, regions of plastic deformation were observed, indicating that GNDs were present. The grain impingement regions in Figure 6.7 are labelled as “1” and results suggest that impingement causes the formation of GNDs. Regions labelled as “2” are regions which do not suffer from any impingement but still exhibit signs of a plastic deformation gradient. This suggests that GNDs can also form during grain growth.

![GAM map of partially crystallised poly-Si(n+)/poly-Si(i) sample. The black regions are a-Si:H and the coloured regions are the poly-Si grains. Regions of grain impingement are labelled “1” and defective growth regions are labelled “2”. The thick white lines around region “1” represent grain boundaries between three grains. The fine red lines are the Σ 3 boundaries. Regions of plastic deformation can be observed in this partially crystallised sample, suggesting that plastic deformation occurs during grain growth as well as during grain impingement.](image)

During SPC, a-Si:H is transformed into poly-Si which has a higher mass density and hence occupies a smaller volume. This introduces tensile stress to the surrounding a-Si:H matrix and the poly-Si phase itself [35]. The tensile stress may have caused plastic deformation and hence the formation of GNDs.
The same perspective can be used for the impingement effect. Prior to impingement between two grains, the remaining a-Si:H between the two growing grains would be under relatively high tensile stress due to interaction with the adjacent grains. This additional stress might have contributed to plastic deformation and formation of GNDs as well.

Figure 6.8. Cross section HAADF-STEM image of the partially crystallised stacked sample. The top part of the grain extends longer compared to the lower part, suggesting preferential growth along the top surface. This could suggest that anisotropic growth mode may have caused plastic deformation.

Figure 6.8 shows that the top part of the grain extends longer than the bottom part of the grain. This suggests that grains preferentially grow along the top part of the film, which is the $n^+$ doped region. Based on Figure 6.7 and Figure 6.8, the anisotropic growth mode seems to be correlated to the formation of plastic strain in poly-Si during SPC. However, a single layer $n^+$ doped film (not shown) was further examined, where anisotropic growth is not expected. In this single layer $n^+$ doped film, misorientation gradients of similar
behaviours as the stacked layers (in Figure 6.4) were still observed, suggesting that the anisotropic growth effect can be eliminated as a root cause for plastic strain.

For the stacked sample, it was noted from Figure 6.4 that the majority of the grains have a core of < ~3 µm which has little or no misorientation gradients (and hence little or no GNDs). The poly-Si(i) films in Figure 6.3 have an average grain size of only ~2 µm and most of the grains do not exhibit any plastic deformation. However the few larger grains (with size of ~3 µm), such as the one demonstrated in Figure 6.3a and Figure 6.3b, do show slight misorientation gradients. This could suggest that the introduction of GNDs is not due to the incorporation of P dopants but rather, more related to the grain size. It is well known however, that doping enhances the growth rate of the grains [36, 37] resulting in larger grains. Hence doping plays an indirect role in this manner.

We report that GNDs start to form for grain sizes of > ~3 µm and depending on fabrication conditions, this threshold of GND formation might change. SSDs are always present in poly-Si material and for larger grains, contribution from GNDs become important as well. Our work could explain why no major improvements in PV device performance were observed for larger grained SPC poly-Si materials [38]. More work is required to minimise not only SSDs in poly-Si but also to prevent the formation of GNDs in the material.

6.6 Conclusions

Electron backscatter diffraction (EBSD) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were used to characterise dislocations in polycrystalline silicon (poly-Si) thin films. Both geometrically necessary dislocations (GNDs) and statistically stored dislocations (SSDs) were identified in the
poly-Si material. It was found that in poly-Si with grain sizes of < ∼3 µm, little or no plastic deformation was found. The dislocations present were mainly SSDs. For poly-Si with grain sizes of > ∼3 µm, measurements from EBSD indicate that plastic deformation in the grains have occurred. In addition, the presence of low angle grain boundaries (LAGBs) consisting of GND arrays were observed. The GND arrays can form at elevated temperatures where GNDs rearrange into a lower energy configuration. Results suggest that the introduction of GNDs were most likely associated to the grain size rather than doping effects. However, since doping is known to enhance growth rate and hence grain size, the doping has an indirect effect in this manner. EBSD analysis of partially crystallised poly-Si revealed that GNDs may be formed during grain growth as well as during grain impingement. To improve crystal quality of the material, either the grain sizes have to be limited to < 3 µm or methods have to be developed to raise the grain size threshold for GND formation.

Acknowledgements

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References


[33] Theoretical Framework for Electron Backscatter Diffraction


Publications related to this chapter:

Chapter 7 On the Transient amorphous Silicon structures during Solid Phase Crystallisation

In this work, we found evidence of an evolving amorphous silicon (a-Si) structure during solid phase crystallisation. Detailed structural analysis of the a-Si material during SPC revealed an increasing bond angle distortion from the ideal crystalline silicon (c-Si) bond angle of 109.5°. In addition, infrared measurements indicated a change in Si-Si bond polarisability. However both their roles in SPC are not yet clear. This preliminary study provides a new insight into the SPC process, which may be essential for future studies.
7.1 Introduction

Solid phase crystallisation (SPC) of amorphous silicon (a-Si) has been the subject of extensive study over the past few decades [1-5]. SPC typically involves annealing of a-Si at ~600 °C for around 10 hours and the resulting polycrystalline silicon (poly-Si) thin film exhibits better electrical properties resulting in more stable device performance as compared to a-Si thin films. Poly-Si thin film solar cells have the potential for cost reduction in photovoltaics since this technology features robust monolithic module design with the use of stable, non-toxic and abundant materials [6, 7]. However, a complete understanding of the SPC process is still lacking and improvement in the fundamental understanding of the SPC process will facilitate improvement in the SPC poly-Si film quality as well as its manufacturability.

The focus of earlier work was on the evolution of the poly-Si phase during SPC [1, 8, 9] and little attention was paid to the changes in structural properties of the a-Si phase during SPC. The main focus of this research is therefore on the evolving a-Si material properties during the SPC process. It is important to consider that the full system is in solid state during crystallisation. In addition, the poly-Si and a-Si phases maintain material continuity during the process and the poly-Si and a-Si phases have a different mass density [10]. Hence the a-Si phase may be subjected to continuous change in structural properties during the SPC process when the poly-Si fraction increases. We have therefore examined the structural and optical properties of the partially crystallised films to gain insights into the changing a-Si structure during SPC.
7.2 Experimental details

An intrinsic hydrogenated amorphous silicon (a-Si:H) film (~1 µm) was deposited on a silicon nitride (SiNₓ, ~75 nm) coated borosilicate glass substrate (30 cm x 40 cm). The a-Si:H layer was deposited using RF-PECVD (MV Systems, USA) at a substrate temperature of 360°C, a SiH₄ flow of 40 sccm, a deposition pressure of 0.6 Torr and a RF power density of 33 mW/cm². Subsequently the centre 6 cm × 6 cm portion of the 30 cm × 40 cm sample was selected for further analyses. The uniformity of the sample was checked by taking 21 measurements by spectroscopic ellipsometry (Sopra GES5E, France). The dielectric function of the a-Si:H film was modelled using a Tauc-Lorentz model [11] while the dielectric function of the SiNx film was modelled using a Cauchy model [12]. The analyses confirmed that the dielectric functions of the a-Si and SiNx film were constants over the 6 cm × 6 cm, while the thickness variation was within 1%. Subsequently, 1 cm × 1 cm samples were cut from the uniform 6 cm × 6 cm sample for the detailed analyses of the SPC process. The SPC dynamics of the a-Si:H film was studied using high-temperature in-situ X-ray diffraction (XRD, Panalytical X’pert Pro XRD, the Netherlands, equipped with Anton Paar HTK 1200N high temperature chamber). The sample temperature was set at 600°C and the chamber pressure was maintained at 7.5 × 10⁻⁵ – 7.5 × 10⁻⁶ torr. More details of in-situ XRD can be found in Chapter 3 of this Thesis.

Raman spectroscopy (Renishaw, inVia, UK) was used to determine the bond angle distortion (∆θ) in a-Si as well as the crystallisation fraction of the samples during the SPC process. An argon light source with a centre wavelength of 514 nm, a power below 50 mW and a spot size of ~20 µm was used. A laser power below 50 mW is required to prevent crystallisation of the sample during the Raman measurement. The measurements were taken 1 – 2 mm away from the edges of the samples to avoid
regions affected by edge induced crystallisation. The crystallinity levels were typically higher closer to the edges due to edge induced crystallisation and the a-Si peak could not be properly deconvoluted at high crystallinities due to a low signal-to-noise ratio at Raman crystalinity levels > 45%. The regions affected by edge induced crystallisation were small compared to the rest of the film and did not affect the SPC kinetics of the rest of the sample. From the literature, it is well known that the full-width at half maximum (FWHM) of the transverse optical (TO) mode at peak position ~480 cm\(^{-1}\) increases with bond angle distortion [13-16]. The bond angle distortion is defined as the root-mean-squared (RMS) bond angle deviation from the c-Si angle of 109.5° [13]. The conversion from TO mode FWHM to bond angle distortion was discussed in Section 3.2.5. The Raman fraction of crystallinity \(f_R\) is defined as

\[
f_R = \frac{I_{Rc}}{I_{Ra} + I_{Rc}},
\] (7.1)

where \(I_{Rc}\) is the sum of the area of all Raman peaks associated with the c-Si phase, which consist of peaks centred between 517 and 519 cm\(^{-1}\) [17]. \(I_{Ra}\) is the Raman peak area associated with a-Si centred around 480 cm\(^{-1}\). It has to be noted that the crystallinity obtained from XRD and Raman spectroscopy are not directly comparable due to the different scattering efficiency ratios of the two phases. The Raman crystallinity can be translated to better represent the actual crystallinity following [18]

\[
f = \frac{I_{Rc}}{I_{Rc} + yI_{Ra}}
\] (7.2)

where \(y\) was reported to be between 0.4 – 1.1.
In this chapter, the fraction of crystallinity obtained from Raman spectroscopy will be referred to as Raman crystallinity and the fraction of crystallinity obtained from XRD will be referred to as XRD crystallinity.

The TO peak FWHM were obtained for samples with varying levels of Raman crystallinity. Multiple samples were annealed at 600°C and taken out of the chamber after various annealing times in the 30 to 450 min range. The annealing chamber used for the Raman spectroscopy experiments was the same chamber used for the in-situ XRD measurement. The cooling time from 600 to 300°C was 9 minutes, where the sample was considered to be kinetically stable. The cooling rate is much faster compared to the rate of structural change during annealing, hence, can be considered as a snap shot of the a-Si structure when the heating was stopped. In addition, Takimoto et al. [19] showed that a-Si thin films with hydrogen removed via annealing have the same thermal expansion coefficient with poly-Si thin films. Any stresses due to the difference in thermal expansion coefficients from the two phases will be negligible.

Fourier transform infrared (FTIR, Perkin Elmer Spectrum 400, USA) spectroscopy in the near-infrared (NIR) region of 1500 – 1950 nm was used in the transmission mode to obtain the refractive indices of the amorphous, partially crystallised and full crystallised samples. In this wavelength range, both the silicon films and SiNx refractive index can be modelled using the Cauchy dispersion relation and the extinction coefficient can be assumed to be zero. The refractive index of the glass and the SiNx film were extracted by spectroscopic ellipsometry measurements on samples that underwent an identical thermal treatment. Subsequently, the a-Si refractive index and thickness can be determined from fitting the fringes in the transmission spectrum following the method published by Swanepoel et al. [20].
The mass density of a-Si:H films can be estimated from the refractive index at long wavelengths based on the Clausius-Mossotti relation [21]:

$$\rho = \left( \frac{n_{tr}^2 - 1}{n_{tr}^2 + 2} \right) \frac{3m_{Si}}{4\pi \left[ 2\alpha_{Si-Si} + \frac{C_H}{1-C_H} \left( \alpha_{Si-H} - \frac{1}{2}\alpha_{Si-Si} \right) \right]}$$  \hspace{1cm} (7.3)

where \(n_{tr}\) is the refractive index at long wavelengths, \(C_H\) the hydrogen content and \(m_{Si}\) the atomic mass of silicon. For the a-Si:H system, the concept of bond polarisability was employed, where the electrons reside between the atoms. \(\alpha_{Si-Si}\) and \(\alpha_{Si-H}\) are the polarisabilities of the Si-Si and Si-H bonds which are \(1.96 \times 10^{-24}\) cm\(^3\) and \(1.36 \times 10^{-24}\) cm\(^3\), respectively [22].

The hydrogen content of the a-Si:H film in this study was estimated using transmission mode FTIR in the mid-infrared (MIR) region (400 – 4000 cm\(^{-1}\)). Using the identical deposition conditions, an a-Si:H film of ~500 nm was deposited on a 10 – 20 Ω cm c-Si <100> wafer with a native oxide interface. The hydrogen content was extracted using the method of Kageyama et al. [23]. The two infrared (IR) absorption peaks generally observed at ~2000 cm\(^{-1}\) and ~2080 cm\(^{-1}\) were assigned to the SiH and SiH\(_2\) stretching modes, respectively. The hydrogen content contribution from each stretching mode is then given by:

$$C_H = \frac{A}{D} \int \omega^{-1} \alpha(\omega) d(\omega) \times 100 \text{ at.} \%,$$  \hspace{1cm} (7.4)

where \(A\) is a proportionality constant which is \(9 \times 10^{19}\) cm\(^2\) and \(2.2 \times 10^{20}\) cm\(^2\) for the SiH and SiH\(_2\) bond states, respectively [24]. \(D\) the atomic number density of a-Si:H assumed to be \(5.2 \times 10^{22}\) cm\(^{-3}\). \(\alpha(\omega)\) the absorption coefficient and \(\omega\) the wavenumber.

The hydrogen content was obtained by adding the \(C_H\) for the two IR stretching modes.
and it was found to be ~6.9 at.%. The SiH mode contributed ~6.2 at.% while the SiH₂ mode contributed only ~0.7 at.%.

For all annealing experiments, the temperature profile up to 600°C was carefully controlled and is shown in Figure 7.1. The plateau at 450°C for one hour prevented film damage from rapid hydrogen out-diffusion and the ramp rates were optimised to prevent damage from rapid thermal expansion. For simplicity, both hydrogenated amorphous silicon and dehydrogenated amorphous silicon will be referred to as a-Si from here on and the growing polycrystalline silicon phase will be referred to as poly-Si.

Figure 7.1. Sample temperature and XRD fraction of crystallinity as a function of time. Various stages of the SPC process can be identified as indicated in the figure. Stage A is the ramp-up stage where the temperature is brought up to 600°C in a controlled way. Stage B is the incubation stage, which is the period of apparent inactivity before crystallisation. Stage C is the period where crystallisation occurs and stage D is the saturation stage where the phase transformation slows due to depletion of the parent a-Si phase.
7.3 Results and discussion

7.3.1 a-Si structural evolution during SPC

Raman spectroscopy was used to monitor the a-Si structural evolution during the SPC process. From the deconvoluted Raman spectra, the FWHM of the TO peak centred at 480 cm\(^{-1}\) was obtained as function of Raman crystallinity and subsequently translated to better represent the actual crystallinity using Eq. (7.2) (with a \(y\) value of 0.4). There was no observable crystallinity for annealing times < 300 min. In Figure 7.2, the FWHM of the TO peaks are only given for the samples that were annealed for > 300 min. As-deposited samples were included in the figure as well as a reference. A total of four samples were analysed and each sample was measured at nine different points to obtain a spread in crystallinity. The TO peaks were monitored up to a level of \(~70\%\) crystallinity. At higher crystallinities, the signal-to-noise ratio for the a-Si peaks was insufficient to allow a proper deconvolution of the TO peak.

![Figure 7.2. TO peak FWHM as a function of crystallinity. A total of 36 measurements were done on four samples. The trend shows an increase of TO peak FWHM with the crystallinity.](image-url)
Figure 7.2 shows an increase in the TO peak FWHM as a function of the crystallinity and indicates that in a sample with higher crystallinity, the surrounding a-Si matrix would be at a higher bond angle distortion.

As-deposited a-Si samples showed a TO peak FWHM of ~67 cm\(^{-1}\) and in the literature this value corresponds to a-Si in a relaxed state [25]. Further annealing up to 300 min did not result in observable changes in the TO peak FWHM. The relatively high temperature of 360 °C used during the PECVD a-Si deposition probably assisted with the relaxation of the a-Si film during deposition due to enhanced diffusion of surface Si atoms. For the sample that was annealed for 300 min, an increase in the TO peak FWHM was observed for all nine measured spots even though the crystal fraction in the seven measurement spots was below the detection limit of our Raman system. The other two points showed ≤ 10% crystallinity. This observation indicates that a relatively low crystallinity fraction is sufficient to cause changes in the RMS bond angles in the a-Si matrix. The sample annealed for 360 min showed a similar TO peak FWHM compared to the sample annealed for 300 min while for samples annealed for 380 min, the TO peak FWHM starts to increase up to a value of ~75 cm\(^{-1}\). This could indicate that the early inclusions of poly-Si for the samples annealed for 300 min caused an initial disruption in the bond angles which are stabilised up to an annealing time of 360 min. For a longer annealing time, for a higher crystallisation fraction, the a-Si matrix is further disrupted with the growth and further inclusion of poly-Si.
7.3.2 Effect of poly-Si inclusions

To investigate the mechanism responsible for the increasing bond angle distortion in the a-Si films with crystal fraction, a few aspects related to the SPC process have to be considered. Firstly, it was assumed that during SPC, the a-Si and poly-Si phases have to maintain material continuity to allow the growth of the poly-Si phase. Secondly, theoretical and experimental work showed that the Young’s modulus of poly-Si can be up to two times that of a-Si, with values of ~170 GPa and ~80 GPa respectively [26-28]. Thirdly, the density of poly-Si is higher than that of a-Si with values of 2.33 g cm\(^{-3}\) and < 2.30 g cm\(^{-3}\), respectively [10].

Stress could be a possible reason for the increasing bond angle distortion and the stress state of the a-Si matrix during SPC can be predicted using the Eshelby’s approach to inclusion problems in a matrix [29, 30]. The procedure is as follows: 1) A region of interest is removed from a-Si matrix, leaving behind a cavity. 2) The removed a-Si region is allowed to undergo an unconstrained transformation into poly-Si. Since poly-Si has a higher density, it occupies a smaller volume. 3) An external surface traction (tensile stress) is applied to restore the poly-Si to original dimensions and placed back into the cavity of the a-Si matrix. The poly-Si is allowed to rejoin the a-Si matrix at the interface. The a-Si matrix at this stage is stress free but the poly-Si inclusion is under tensile stress. 4) Finally, the applied external force on the poly-Si inclusion is allowed to relax, with equal and opposite force applied on the a-Si matrix.

Therefore it can be concluded that the a-Si matrix was under tensile stress with the inclusion of poly-Si phases and as the SPC progresses, the a-Si matrix was increasingly under more tensile stress. In addition, since poly-Si is embedded inside the a-Si matrix, it does not relax fully and should also be in a state of tensile stress as well. This conclusion can be validated by the results of Fu et al. obtained for nanocrystalline Si.
films [31], where the stress in the a-Si films became more tensile with the inclusion of more silicon in the a-Si matrix and the stress was reported to be mainly due to nanocomposite effects.

It was found previously that tensile stress leads to a faster SPC rate [2, 32] (higher nucleation and growth rates) and with increasing tensile stress in the a-Si matrix, the SPC rate would be expected to increase as a function of time.

7.3.3 Optical properties of a-Si during SPC

To gain insights into the optical properties of the a-Si film during the SPC process, the overall refractive index of the Si film was analyzed at 1950 nm by transmission mode FTIR. Figure 4 shows $n_{ir}$ of samples at various stages of the SPC process ranging from the as-deposited state at 0 min to the fully crystallised state after an annealing time of 420 min. The stages A to D as defined in Figure 7.1 are demarcated in Figure 7.3 as well.
Figure 7.3. The refractive index of the Si film as a function of annealing time of the sample. Stages A – D are indicated similar to Figure 7.1. The solid line shows the EMA approximation of the refractive index of the Si film as a function of the annealing time using the XRD crystal fraction as an input for $f$ in Eq. (7.5).

At the end of stage A (after an annealing time of 180 min), it was found that the refractive index of the Si film increased from 3.48 to ~3.76. During this stage, the increase in refractive index could be related to the densification of the films as hydrogen diffuses out of the Si film and the void structures in the a-Si film changes [33-35].

In stage B, no change in the refractive index of the Si film was detected for samples annealed for 180 and 240 min. The mass density of the a-Si film obtained from the Clausius-Mossotti relation [Eq. (7.3)] assuming $C_H = 0$ at.% was $\sim 2.30$ g cm$^{-3}$, which is close to the values of 2.29 g cm$^{-3}$ reported for a-Si films with $> 99\%$ of hydrogen removed [36]. For the sample annealed for 300 min, a strong increase in refractive index of the a-Si film to ~3.92 was detected. Around this annealing time the formation of initial quantities of poly-Si crystals was detected by both XRD and Raman spectroscopy. It
was observed that after the initial increase after an annealing time of 300 min, the refractive index of the Si film starts to decrease until the completion of SPC process after an annealing time of 420 min. A refractive index > 3.9 for an a-Si film close to the transition from a-Si to poly-Si was also reported for Si films deposited by low pressure chemical vapour deposition [37]. It is likely that the inclusion of the first poly-Si crystals caused significant disruption in the a-Si network resulting in changes in the refractive index.

From stage C onwards, the refractive index of the Si film starts to decrease towards the expected value ~3.5 for poly-Si thin films [37].

To understand the changes in the refractive index of the Si film as a function of the annealing time a simple effective medium approximation (EMA) [38] was used. Here the EMA approximation is given by:

\[
(1 - f) \left( \frac{\varepsilon_{\text{a-Si}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{a-Si}} + 2\varepsilon_{\text{eff}}} \right) + f \left( \frac{\varepsilon_{\text{poly-Si}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{poly-Si}} + 2\varepsilon_{\text{eff}}} \right) = 0
\]  

(7.5)

where \( f \) is the fraction of crystallinity, \( \varepsilon_{\text{eff}} \) the effective dielectric function of the crystallising Si film, \( \varepsilon_{\text{a-Si}} \) and \( \varepsilon_{\text{poly-Si}} \) the dielectric functions of a-Si and poly-Si respectively. In the IR wavelength range the extinction coefficient \( k \approx 0 \) and \( n_{ir} \approx \sqrt{\varepsilon_{\text{eff}}} \).

In our EMA calculation, the refractive indices of the parent a-Si phase and poly-Si phase were fixed at 3.75 and 3.54, respectively, throughout the entire range of crystallinity and the EMA fit is indicated in Figure 7.3 as well using the XRD crystallisation fraction from Figure 7.1 as input for \( f \).

Since the refractive index of poly-Si was lower than a-Si, the EMA approximation predicts a trend of decreasing \( n_{ir} \) for an increasing crystal fraction. However, the
experimental data in Figure 7.3 shows a clear deviation from this trend. Basically the EMA approximation is unable to account for the evolution of the refractive index during the whole crystallisation phase. In the EMA approximation, both the a-Si and poly-Si phases were assumed to have a constant refractive index throughout the SPC process. Following Eq. (7.3), the assumption of a constant refractive index implies constant mass density, constant Si-Si bond polarisability and constant stress [39, 40] of each phase during SPC, which may not be the case. Since it was shown earlier that the a-Si matrix and poly-Si phase were under tensile stress, it is highly unlikely that the mass density of either phase could significantly increase, hence, an increase in mass density as root cause for the $n_{ir}$ increase can be excluded.

To analyse the change in polarisability of Si-Si bonds in the films during SPC, it was first assumed that the polarisability change was completely due to the a-Si phase. Using Eq. (7.3) and using mass densities of 2.30 g cm$^{-3}$ and 2.33 g cm$^{-3}$ for a-Si and poly-Si, respectively, the increase in $n_{ir}$ of the mixed phase Si film from 3.75 to 3.92 would result in a change in polarisability of Si-Si bonds in a-Si from $1.96 \times 10^{-24}$ cm$^3$ to $2.00 \times 10^{-24}$ cm$^3$. From this result, it was also calculated that the refractive index of the a-Si phase itself would be as high as 3.95 and calculations of the a-Si refractive index at even higher crystal fractions yielded values which are no longer reasonable. Hence it can be concluded that the polarisability of the Si-Si bonds in poly-Si should also be increasing during SPC together with the polarisability of Si-Si bonds in a-Si. It is however not clearly understood how the polarisability change is related to the structural properties of a-Si.

7.4 Conclusions

In this work, the a-Si structure was probed during SPC using Raman spectroscopy and FTIR. We found evidences of evolving a-Si structures during the SPC process. From Raman spectroscopy, we observed an increasing bond angle distortion compared to the
ideal c-Si angle of 109.5° during the course of the SPC process. FTIR also revealed increase in Si-Si bond polarisability in a-Si during SPC. However the roles of both bond angle distortion and bond polarisability in SPC are still not clear at this moment and could be a subject for further study. This insight in the SPC process could be crucial in the optimisation of the poly-Si material quality for photovoltaic applications as more care can be taken on the evolving a-Si structure during the SPC process in the future.

References


**Publications related to this chapter:**

Chapter 8 Conclusions and Future Work

8.1 Conclusions

In this Thesis, the various stages of the solid phase crystallisation (SPC) process were investigated to obtain better fundamental understanding, with the goal of attaining better control over the process and achieving high efficiency polycrystalline silicon thin film solar cells on glass.

Building on the recent advances in understanding the hydrogenated amorphous silicon (a-Si:H) structure, an anisotropic view of the a-Si:H structure was adapted and related to the SPC process and the final poly-Si material quality. In the anisotropic a-Si:H material, regions of higher ordering were taken to be the nucleation sites and the number density of these nucleation sites are referred to as the nucleation site density. The apparent Avrami exponent \( n \) was used empirically to group the a-Si:H materials into two types, namely, \( n < 4 \) and \( n > 4 \). \( n < 4 \) a-Si:H material yielded small defective grains with a non-robust SPC process while \( n > 4 \) a-Si:H material yielded large columnar grains of better quality with more robust SPC process. From our observations, \( n > 4 \) a-Si:H material were preferred.

By utilising the expanding thermal plasma (ETP) and radio frequency parallel plate plasma enhanced chemical vapour deposition (RF-PECVD) techniques, different types of a-Si:H precursors were available for study. Certain ETP and RF-PECVD a-Si:H films had similar \( n \) values but the ETP a-Si:H films have longer incubation times and slower crystallisation rates during SPC. Against intuition, the average grain sizes of the ETP poly-Si were found to be much smaller than the RF-PECVD poly-Si. It was interesting to
observe that the average grain sizes of the poly-Si films were not solely affected by the SPC dynamics and most likely the nucleation site density plays a role in determining the grain density (and hence average grain size) as well.

There is a consensus in the research community that the medium range order (MRO) has an effect on the SPC dynamics and our results suggest that an a-Si:H precursor with lower MRO is more suitable for SPC poly-Si. Even though H₂ dilution of SiH₄ is known to improve the MRO in a-Si:H, the means to reduce MRO in RF-PECVD a-Si:H films is not well investigated. It was found that lowering deposition pressures can reduce the MRO of the deposited a-Si:H. Transmission electron microscopy and UV reflectance measurements revealed that a-Si:H precursors with lower MRO yielded poly-Si grains which are of higher crystallographic quality.

The dislocation density in poly-Si derived from SPC of a-Si:H cannot be well controlled. In our work, the results suggest that additional dislocations in the form of geometrically necessary dislocations may form during SPC, which indicate that plastic deformation has occurred. The plastic deformation is most likely due to stresses in the system during SPC, which is hardly surprising considering that the entire system is in solid phase: localised changes in film density due to nucleation and growth of denser poly-Si embedded within the amorphous silicon parent phase (a-Si) may have introduced stress into the system.

To gain insights into the SPC process, the a-Si properties were monitored throughout the SPC process. Reduction in short range order (SRO) was observed together with more inclusion of poly-Si material (increasing crystallinity). Change in Si-Si bond polarisability was also detected via FTIR. These observations are not well understood and remain to be studied in more details.
With this Thesis, we gained a better understanding of the SPC process to fabricate poly-Si thin film on glass. This brings us closer to achieve the goals of better control over the SPC process and higher efficiency poly-Si thin film solar cells.

8.2 Future work

The understanding of SPC of a-Si:H for applications in thin film silicon solar cells is far from complete, with the challenging issue of dislocation density control still not solved. Dislocation density control is a key to improve poly-Si thin film solar cell efficiencies. This Thesis has provided better understanding and more insights into the SPC process which hopefully serves as a guide for future research into reduction of dislocation densities.

The following paragraphs discuss briefly the possible research focus for further development of the poly-Si thin film solar cell technology.

While results from scanning transmission electron microscopy seem to indicate that lower $n$ values yielded grains with poorer crystallographic quality and higher grain densities, results on electrical performances are still required to complete the picture. It is noted that for analyses of electrical performances, PV devices typically need to be fabricated which complicates the fundamental research. For example, a typical poly-Si thin film solar cell involves a pre-SPC structure of glass/SiN/$n^+$ a-Si:H/$p^-$ a-Si:H and it is not known how each individual layer would affect the overall SPC behavior and the final poly-Si quality.

We found that dopants may enhance growth rates which lead to grains > 3 µm and the incorporation of GNDs, however the effect of dopants (doping types and concentrations) on the concentration of statistically stored dislocations (SSDs) have not been well studied. While GND concentration can be minimised by limiting the grain sizes to < 3 µm,
there is limited work on how SSDs can be minimised. Minimising SSD incorporation during SPC should be explored as well.

While we found that lower deposition pressures can lead to reduced MRO, other parameters, such as temperature, power, electrode spacing, precursor gas flow rate and the utilisation of other precursor gases (e.g. Si₂H₆), remain to be studied. To enhance the understanding, plasma physics and chemistry associated with each changing parameter needs to be investigated with the utilisation of plasma diagnostics. Information such as the plasma potential, the amount of ion bombardment, the radical and ion species present in the plasma etc., are essential to realise full control over the precursor a-Si:H properties. Ultimately, it would be ideal to achieve reduced MRO for a-Si:H films with deposition parameters which allow large area uniform deposition with a high deposition rate to improve the throughput. The current focus should be on the 13.56 MHz PECVD technique which benefits from the developments for the display industry, until another deposition technique proves to fabricate better suited a-Si:H materials for SPC poly-Si at large area. At the current state of knowledge, even the structure of the preferred a-Si:H has not been clearly identified and this could be the subject of further investigation.

Having identified GNDs in poly-Si material which indicates the presence of plastic deformation in SPC poly-Si, it becomes clear that stress engineering during SPC should not be neglected as it may be closely related to dislocation density in poly-Si. Topics of interest we identify in this area include 1) a deeper study of the Eshleby’s problem of inclusion – nucleation and growth of poly-Si is akin to introducing particles of higher mass density in a matrix of less dense parent a-Si phase. This introduces tensile stress in the system and work should aim towards minimising this effect, i.e. fabricating very high density a-Si:H to minimise the mass density difference between a-Si:H and poly-Si
may help; 2) optimising temperature-time profiles (heating up and cooling down) which minimise stress on the film; 3) the investigation of buffer layers between the glass substrate and the silicon films which may help reduce stress; last but not least, 4) the stress effect of different substrates (e.g. metal foil VS glass).

8.3 Contributions from author

The following highlights the contribution of this Thesis

- Developing optimised measurement recipes for in-situ XRD measurements of the SPC dynamics of a-Si:H on glass. Parameters optimised were the XRD signal acquisition time and step size. A longer acquisition time leads to higher signal-to-noise ratio but on the other hand, a faster scan time is required so that the phase transformation do not proceed faster than the measurement time. Care was taken to optimise the step size for different samples. For example, the XRD peaks for ETP poly-Si films are in general broader compared to RF-PECVD poly-Si films, hence for ETP samples, larger step sizes and longer acquisition time per step are possible. For RF-PECVD poly-Si, XRD peaks are in general narrower and step sizes have to be smaller and consequently acquisition time per data point has to be reduced.

- The author extended the EBSD capability to identify plastic deformation in poly-Si thin film material which manifest in the form of GNDs. While EBSD has been applied to poly-Si thin film materials, prior work was mainly to extract the average grain sizes and to delineate the grain boundaries.

- Setting up Secco etching (0.15 M K$_2$Cr$_2$O$_7$ and 49% HF at 1:2 ratio by volume, respectively) capabilities at SERIS for delineating grain boundaries in poly-Si thin
film material. The author established a procedure to optimise the etching time to reveal grain boundaries in poly-Si material.

- Demonstrated Fourier Transform Infrared (FTIR) in the attenuated total reflection (ATR) mode to study a-Si:H on glass. This allows fast and non-destructive diagnostics of a-Si:H prior to the SPC process.

- Together with A*STAR DSI, the author explored and utilised HAADF-STEM to image dislocations in poly-Si. It has been shown in the literature that HAADF-STEM can image dislocations but mainly applied for Si wafers. This method is relatively fast compared to conventional TEM methods and upon comparison, HAADF-STEM seems to have better resolution.
Journal publications related to this Thesis


Conference proceedings
