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# Formation of thin-film crystalline silicon on glass observed by insitu XRD

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## Abstract

Thin-film poly-crystalline silicon (poly c-Si) on glass obtained by crystallization of an amorphous silicon (a-Si) film is a promising material for low cost, high efficiency solar cells. Our approach to obtain this material is to crystallize a-Si films on glass by solid phase crystallization (SPC). As the grain size of SPC poly c-Si films will be smaller than that of multi-crystalline wafers, lower solar cell efficiencies are expected for this technology. Despite the smaller grain size, a 2-micron-thick polycrystalline silicon solar cell with light trapping was shown to have a conversion efficiency of more than 10% [1]. Obtainable efficiencies up to 15% are expected for solar cells made using SPC of a-Si:H films. Expanding thermal plasma chemical vapor deposition (ETP-CVD) was used to prepare hydrogenated a-Si films; this technique is chosen because the deposition rates are much higher than with plasma enhanced CVD. A-Si:H films with different hydrogen contents were annealed using temperatures ranging from 500°C to 700°C. The evaluation of the films after annealing treatments revealed that the hydrogen content and bonding configuration did not influence the structural properties of the crystallized films significantly. The average crystallite within 20 minutes for annealing at 625°C and 650°C. During annealing at 600°C crystallization is much slower, and no crystallization is observed at 500°C. The relation between the annealing temperature and the rate with which the films are fully crystallization is observed at 500°C.

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## 1. Introduction

Today's terrestrial PV market is dominated by crystalline silicon (c-Si) solar cells based on wafer technology, which accounts for almost 90% of the world solar-cell production [2]. In order to maintain the rapid expansion of the solar cell sector, reduction of the cost of c-Si solar modules is required. This module price is dominated by cost of the c-Si wafers. A significant cost reduction can be achieved by reducing the consumption of highly pure silicon [3]. For this reason the investigation of poly c-Si thin films on glass has received a lot of attention recently [4]. Several methods can be used to obtain a thin poly c-Si film from amorphous silicon (a-Si) deposited on glass, like aluminum induced crystallization, laser induced crystallization and solid phase crystallization [5, 6]. The a-Si films can be deposited by techniques such as plasma-enhanced chemical vapour deposition (PE CVD) and e-beam

evaporation. For this approach to become a viable technology, both the deposition conditions and the annealing treatment should be optimized in order to minimize the energy consumption during production and achieve a high solar cell performance.

The maximum temperature of the annealing treatments for industrial solar cell production should be limited to about 650°C, which is the glass softening temperature. An additional advantage of lower temperatures for processing is that it reduces the thermal budget and the thermal stress induced by the annealing treatment. In this article intrinsic poly c-Si films were obtained by annealing hydrogenated amorphous silicon (a-Si:H) films, deposited by expanding thermal plasma chemical vapour deposition (ETP CVD). ETP CVD is used for the fast deposition of a-Si:H films; with this technique a-Si:H films can be grown at deposition rates up to 11 nm/s [7]. Another advantage is that ETP CVD is a remote plasma technique, allowing for independent control of the plasma and substrate conditions.

We studied the influence of the annealing temperature on the rate of the phase transition for temperatures in the range between 500 and 700°C. We also investigated the effect of the hydrogen content and the hydrogen bonding configuration on the phase transition from a-Si:H to poly c-Si. For application in solar cells the poly c-Si will need to be doped. However, this study is limited to intrinsic material, which will enable us to investigate the effect of doping later.

In section 2 we describe the details of the deposition technique, the measurement techniques employed and the annealing procedures. We will then present and discuss our results of the different annealing profiles on the crystallization in section 3 and 4. In the discussion we will also pay attention to the average crystallite sizes of the poly c-Si films in the discussion.

## 2. Experimental details

The a-Si:H films were deposited by ETP-CVD method. This deposition method was developed by Eindhoven University of Technology and has been described in detail before [8, 9]. ETP CVD is a remote plasma technique in which DC Ar-H<sub>2</sub> plasma is created in a narrow channel of a cascaded arc at a pressure of approximately  $45 \times 10^3$  Pa. The current in the arc is 40 A. The plasma subsequently expands through a nozzle into the deposition chamber, which is at a pressure of approximately 20 Pa. In this chamber silane (SiH<sub>4</sub>) is injected into the plasma beam and an a-Si:H film is deposited on a temperature-controlled substrate approximately 40 cm downstream. The a-Si:H films were deposited on Eagle 2000 Corning glass and on c-Si (boron doped prime CZ wafer with <100> orientation). The deposition conditions during the growth were kept constant except the substrate temperature. The gas flows were: 690 sccm Ar, 340 sccm H<sub>2</sub> and 230 sccm SiH<sub>4</sub>. The film thicknesses were approximately 850, 1000 and 1700 nm.

Fourier Transform Infrared (FTIR) spectroscopy was used to evaluate the hydrogen content and bonding configuration in the a-Si:H films. The integrated absorption of the vibration mode at 640 cm<sup>-1</sup> was used to determine the hydrogen concentration in the film. The modes centered at ~ 1980-2010 cm<sup>-1</sup> and ~ 2070-2100 cm<sup>-1</sup> are called the low stretching mode (LSM) and high stretching mode (HSM), respectively, and were used to determine the microstructure parameter,  $R^*$ . This parameter is a figure of merit for the microstructure of a-Si:H and is defined as:

$$R^* = \frac{I_{HSM}}{I_{ISM} + I_{HSM}},\tag{1}$$

where  $I_{LSM}$  and  $I_{HSM}$  are the integrated absorption strengths of the low and high stretching modes, respectively [10]. An  $R^*$  value below 0.1 is generally found in device quality a-Si:H [10, 11]. The vibration mode at 2000 cm<sup>-1</sup> corresponds to monohydride SiH bonding [12], whereas the 2100 cm<sup>-1</sup> mode was originally associated by Lucovsky [11] to dihydride SiH<sub>2</sub> bonding. Recently, Smets et al. [13] related this mode to monohydride SiH bonding configuration on void surfaces or in multiple vacancies. The hydrogen contents and bonding configuration can be manipulated by the plasma conditions and the substrate temperature during deposition. The deposition temperatures were 200, 300 and 400°C, resulting in hydrogen contents varying from 6.1 to 11.3 at.%, and  $R^*$  ranging from 0.15 to 0.38. Raman spectroscopy was used to investigate the presence of crystalline phase in the layers. From measurements on as-deposited a-Si:H layers we did not detect any crystalline fraction.

The phase transformation of a-Si:H films into poly c-Si film due to an annealing treatment was monitored by insitu x-ray diffraction (XRD). In-situ XRD experiments were carried out in an Anton Paar high-temperature chamber HTK 1200. During the experiments the high-temperature chamber was pumped down to  $2 \times 10^{-1}$  Pa. XRD patterns were collected by a automatic powder diffractometer in symmetric geometry, using Copper K $\alpha$  characteristic radiation ( $\lambda = 0.154$  nm). The irradiated area of the sample was 10 mm × 10 mm. The XRD pattern was measured in 4 minutes for 2 $\theta$  varying from 26 to 31 deg, where the strongest silicon line of <111> orientation is located.

An example of an XRD measurement of poly c-Si on glass, over the full pattern, is shown in figure 1, indicated by the blue line. The example sample was deposited at substrate temperature of 400°C was annealed at 600°C for 8 hours. XRD patterns were preliminary processed using an X'pert HighScore plus software package (background determination and subtraction, removal of the K $\alpha_2$  component). In order to obtain the basic parameters of the lines (2 $\theta$  peak position, intensity, FWHM and integrated intensity), diffraction line profiles were then approximated by a Pearson VII function using a least square procedure. Ex-situ measurements were made with the same equipment, but the range used is 15 to 65 deg of the 2 $\theta$  scale, which includes the three strongest silicon lines. An estimation of the crystallite size was calculated using a procedure that is based on a Voigt function analysis of the widths of diffraction lines (FWHM and integral width  $\beta = area/I_o$ ) proposed by Langford [14], where  $I_o$  is defined as the peak height.



Figure 1. Complete XRD pattern for polycrystalline silicon reference powder (red line), polycrystalline silicon on glass (blue line) showing both the signal from the silicon and the glass background, and red dots indicating the expected line positions.

Two annealing treatments have been used in the in-situ experiments, the profiles of which are shown in figure 2.

- Profile A<sub>F</sub>: is a simple plateau (figure 2a).
- Profile A<sub>8h</sub>: is similar in to A<sub>F</sub> in ramp up, but has a duration of 8 hours (figure 2b).

The first annealing profile ( $A_{F}$ ) is used to evaluate the crystalline phase fraction that develops within 2 hours and in which temperature ranges at which crystallization of the films occurs. The  $A_F$  profile was carried out on four different samples using four different plateau temperatures: 500, 600, 650, and 700°C, to evaluate the influence of temperature on the crystallization process. Profile  $A_{8h}$  was carried out at 600, 610 and 620°C; during these treatments in-situ XRD measurements were carried out each half hour. The samples used for in-situ measurement during profile  $A_F$  had thicknesses of around 1700 nm and a hydrogen content of approximately 6 at.%; for the  $A_{8h}$ profile, samples with a thickness of approximately 1000 nm and hydrogen content around 8 at.% were used.

Ex-situ XRD measurements were carried out on samples with varying hydrogen content and bonding in the amorphous films, which were annealed for 2 hours using the  $A_F$  annealing profile, at 600, 612 and 625°C. An overview of the samples, annealing profiles and temperatures can be found in table 1.



Figure 2. Sketches of the temperature profiles used for the annealing profiles. The circles indicate the time at which the in-situ XRD measurements are made: (a) Ramp up to constant temperature and annealing for two hours. This profile is used also for temperatures from 500 to 700°C; (b) ramp up to constant temperature and annealing for eight hours. This profile is used for temperatures of 600 to 620°C.

#### Table 1. Overview of experiments

Experiment	Annealing profile	Annealing time (hours)	Measurements per sample	Sample thickness (nm)	Plateau temperature (°C)	Deposition temperature (°C)
In-situ	$A_{\rm F}$	2	4	$1700\pm50$	500/600/650/700	400
In-situ	A <sub>8h</sub>	8	16	$1000\pm50$	600/610/620	300
Ex-situ	$A_{\rm F}$	2	1	$850 \ \& \ 1700 \pm 50$	600/612/625	200/300/400

## 3. Results

Figure 3 shows the results of the measurements made during annealing profile  $A_F$  at 500, 600, 650 and 700°C. Each plot shows measurements carried out after the same annealing time at different temperatures. For samples annealed at 650 and 700°C the <111> line intensity saturates. The sample annealed at 600°C shows almost no peak after 45 minutes, but this peak is clearly present after 125 minutes. For annealing at 500°C no <111> line is observed after two hours of annealing.



Figure 3. XRD scans of the <111> line for samples annealed using profile  $A_F$  at temperatures varying from 500 to 700°C: (a) after 45 minutes,  $A_{F1}$  (b) after 85 minutes,  $A_{F2}$  and (c) after 125 minutes,  $A_{F3}$ .



Figure 4. Plots of the integrated intensity of the <111> line as measured by XRD as a function of annealing time during annealing profile  $A_{8h}$ , executed at three different temperatures: 600°C (squares), 610°C (circles), and 620°C (triangles).

After the annealing by profile  $A_F$ , Raman spectroscopy was carried out on these four samples. In the spectra (not shown here) of samples annealed at 650 and 700°C a strong TO peak is present at 520 cm<sup>-1</sup>. The sample annealed at 600°C also shows a peak at this wave number, though in this case also a clear a-Si:H contribution to the Raman spectrum is found. Finally, for the sample annealed at 500°C no c-Si peak at 520 cm<sup>-1</sup> is observed.

Figure 4 shows the measurements made during the  $A_{8h}$  annealing profile at three different temperatures: 600, 610, and 620°C. In this figure the integrated intensities of the <111> line are plotted, which indicate to what extent the transition from amorphous to the crystalline phase is completed. As can be seen, this intensity saturates at a similar level for all three temperatures. The films are assumed to be fully crystalline when reaching this level (as was confirmed by Raman Spectroscopy). The time in which full crystallization is reached, is shortened with increasing annealing temperature.



Figure 5. The integrated intensity of the XRD <111> line as a function of (a) the hydrogen content and (b) the microstructure parameter,  $R^*$ . All measurement results have been normalized to the fully crystalline integrated intensity, and compensated for the sample volumes.



Figure 6. Results of the average crystallite size calculation from XRD patterns of samples deposited at 300°C and annealed using profiles  $A_F A_{Sh}$ , the y-axis is the estimated crystallite size from the XRD patterns, x-axis is the annealing temperature. a) Results from the  $A_F$  profile. b) Results from the  $A_{Sh}$  profile.

Ex-situ measurements were performed after annealing treatments with profile  $A_F$  at a temperature of 600, 612 and 625°C. The samples used for these experiments had different hydrogen contents and bonding configuration (induced by deposition at temperatures of 200, 300, and 400°C). Figure 5(a) and 5(b) the integrated intensities of the <111> lines normalized to the fully crystallized integrated intensity as a function of hydrogen content and  $R^*$ , respectively. For each annealing temperature similar intensities are reached for material with the two lower hydrogen contents and  $R^*$ . For the highest hydrogen content and  $R^*$  the samples deposited at 625°C a lower intensity is found.

We have observed that after annealing treatments at temperatures of 650°C and above the <111> integrated intensity saturates before the first measurements (A<sub>F1</sub>). Annealing at 500°C does not induce any crystallization at all during the flat profile, as is confirmed by Raman spectroscopy. In addition, Raman spectroscopy indicates that films still contain an a-Si:H fraction after annealing at 600°C for two hours. In the samples annealed at 650°C and above no a-Si:H contribution is detected by Raman spectroscopy.

## 4. Discussion

Figure 5 shows the results of the integrated intensity of the <111> line for samples with a variation of hydrogen content and bonding after annealing for 2 hours using the A<sub>F</sub> profile at 600, 612 and 625°C. Effusion before or during the phase transition must be occurring at these temperatures, especially as the solubility of hydrogen in silicon is lower for the crystalline phase than in the amorphous phase [15]. Annealing at 625°C gives a lower intensity, although the Raman spectrum shows no amorphous peaks. The lower XRD integrated intensity could be due to a lower density of the material, which could be caused by hydrogen entrapment. However, we do not have sufficient data to support this explanation. Up to about 8 at.% hydrogen concentration no difference is observed. For highest concentration investigated we observe an anomaly for the sample annealed at 625°C. We have not explanation for this, but we think that this is an artifact.

From the ex-situ experiments at 600, 610 and 620°C and the samples annealed for 8 hours ( $A_{8h}$ ) estimates of the average crystallite size have been calculated. The results of these calculations are shown in figure 7. Although the error margins are substantial, all three series show a decrease in crystallite size with increasing temperature. This observation suggests that apart from the influence of temperature on the crystallization rate, the temperature can also be of influence on the resulting crystallite size. The trend visible in figure 6(a) could be explained by assuming that the rate at which stable nuclei occur, increases with increasing temperature. As these nuclei grow into crystallites, the distance between 2 neighboring nuclei can be the limiting factor for the crystallites to grow. This cannot explain

why the thinner the film has a larger crystallite size. Comparing figures 6(a) and 6(b) it should be noted that results of (a) are after 2 hours of annealing (A<sub>F</sub>) and the layers still hold an amorphous fraction; on the other hand the results after 8 hours (A<sub>8h</sub>) are fully crystalline. The average crystallite size in both experiments is similar, even though amorphous material is still present is the films annealed for 2 hours, annealed at 600 °C.

## 5. Conclusion

A-Si:H films of approximately 850 nm to 1700 nm, deposited by ETP CVD, can be fully crystallized within 2 hours at temperatures in the range of 620 to 650°C. The crystallization rate increases with annealing temperature.

Additionally the results demonstrate that the annealing temperature has a large influence on the rate of phase transition. Hydrogen content and bonding has not been shown to influence the crystallization process, although a lower XRD integrated intensity is observed for the high hydrogen content sample annealed at 625°C, Raman spectroscopy showed no presence of amorphous material in that film.

The average crystallite sizes for fully crystallized and mixed phase films are both in the order of 60 to 170 nm magnitude.

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