ABSTRACT: Solid-phase crystallisation (SPC) of hydrogenated ($H^+$) and dehydrogenated ($H^-$) Si thin films on glass deposited by electron-beam (e-beam) evaporation (EVA) and plasma-enhanced chemical vapor deposition (PECVD) is compared. Four independent film characterisation methods, optical transmission microscopy (OTM), UV reflectance spectroscopy (UV-R), X-ray diffraction (XRD) and Raman spectroscopy, reveal that for the SPC process at 600°C the evaporated films have similar incubation and nucleation times as the PECVD films but the number of initial crystal grains is less and their growth rate is faster in the evaporated films. The scanning electron microscopy (SEM) images of fully crystallised polycrystalline Si film (poly-Si) samples after Secco etching show that the average grain size is larger in the evaporated film. The resulting quality of evaporated poly-Si appears to be at least as good as the quality of poly-Si made by PECVD promising similar cell efficiencies. Hydrogen is not responsible for the observed differences between SPC of the films from two different deposition methods.

Keywords: 1. Poly-Si 1. Solid Phase Crystallisation 2. Si e-beam evaporation 3. a-Si:H PECVD

1 INTRODUCTION

Poly-Si on glass thin-films solar cells is one of promising technologies for lower cost PV electricity generation and for large area applications like building integrated PV [1]. However, glass used as a film substrate or superstrate cannot withstand prolonged treatments at temperatures much higher than its critical points. Hence, shortening of the high temperature processes, such as SPC of amorphous silicon (a-Si) while maintaining a relatively good crystalline material quality, is important for improving the poly-Si on glass cell technology [2].

Most publications on SPC of a-Si are concerned with the hydrogenated a-Si (a-Si:H) formed by PECVD [2-3]. Recently an alternative deposition method of unhydrogenated a-Si by electron beam evaporation has been developed [4], which has such advantages over PECVD as high Si deposition rate (up to 1 µm/min), lower Si source material usage, and avoidance of toxic gases [5]. It can be expected that the evaporated a-Si films crystallise differently, and for the optimum solar cell performance they may require SPC conditions different from those for the PECVD films. To develop such an optimised SPC process, it is essential to achieve a better understanding of the crystallisation stages, such as the incubation, nucleation, and crystal growth, and to identify how these stages and the resulting poly-Si crystal quality differ between evaporated and PECVD films, and a role that hydrogen in the PECVD films plays in SPC.

In this work we compare SPC of the evaporated and the PECVD films by examining samples’ structural material properties by means of optical transmission microscopy (OTM), UV reflectance spectroscopy (UV-R), X-ray diffraction (XRD) and Raman spectroscopy. The results demonstrate that an intermediate stage of the crystal growth proceeds faster in the evaporated films than in the PECVD films with or without hydrogen. The SEM images reveal that after full crystallisation the average grain size in the evaporated film is larger than that in the PECVD film. The findings point at a feasibility of a shorter SPC process for the evaporated films.

2 EXPERIMENTAL PROCEDURE

The substrate for film deposition was planar 3 mm thick Borofloat 33 (from Schott AG) glass coated with about 100 nm thick silicon nitride antireflection and barrier layer. The films of the similar structure shown in Fig. 1 were fabricated by e-beam evaporation and by PECVD.

After the deposition, half of the PECVD film samples were pre-annealed at 450°C in nitrogen ambient to dehydrogenate ($H^-$) them and make more comparable with the un-hydrogenated evaporated films. SPC experiments were performed in a tube furnace in nitrogen ambient at the temperature of 600°C for subsequently increasing times.

3 RESULTS

Fig. 2 shows the OTM images of the evaporated and $H^+$ PECVD films after annealing for 7 hrs indicating more advanced crystallisation in the evaporated films, which have fewer and larger grains than the $H^+$ PECVD films. After annealing for 10 hrs, as shown in Fig. 3, significantly less of the residual amorphous tissue is left in the evaporated films than in the $H^+$ PECVD films. No significant differences are observed between the OTM images of $H^+$ PECVD and $H^-$ PECVD films for all examined annealing times.
One of the commonly used optical methods for analysing a crystalline Si material is the measurement of the hemispherical reflectance in the UV region between 200 and 400 nm [6]. This method is fast and non-destructive, has a large probing area of the order of square centimeters, and a very good reproducibility with error of ±0.001 [7]. Note that UV light has a very small penetration depth (normally below 50 nm) in Si. Therefore, UV-R measurements merely analyse the surface region of Si samples. In this study all the samples underwent a short HF dip to remove the native oxide from the Si surface just before the measurements.

Fig. 4 shows the UV reflection spectrum of standard FZ c-Si wafer exhibiting two prominent maxima at the wavelengths of about 365 nm ("E1") and about 276 nm ("E2"). Structural disorder in the sample surface region causes broadening and height reduction of these maxima. Hence, the UV-R is a measure of the spatially averaged sample crystalline quality [8]. Fig. 4 also defines the Normalised Crystal Quality factor of UV-R (Quv), used to describe and compare the degree of crystallinity of the poly-Si films, where \( \Delta R / R_{\text{sample}} \) and \( \Delta R / R_{\text{c-Si}} \) are the normalised intensities of the peak E2 at 276 nm for a sample and the standard FZ c-Si wafer, respectively [9]. Obviously, the Quv is 0% for a-Si and 100% for the c-Si wafer, and an increase in Quv suggests the improvement of crystallinity in the measured film [6-9].

The XRD patterns for the evaporated and PECVD films after annealing for 8 hrs are displayed in Fig. 6. The patterns exhibit three major diffraction peaks of Miller indices at 2\( \theta \) values of about 28.4°, 47.3° and 56.2°, which are due to the \{111\}, \{220\} and \{311\} Si planes (See the XRD reference data for standard Si power from the Joint Committee on Powder Diffraction Standards [10]). The inset equations in Fig. 6 show the calculation of the Normalised Crystal Quality factor of XRD (Qxrd) for the film. \( I \) and \( I_0 \) are the intensities of the three major diffraction peaks (only \{111\}, \{220\} and \{311\} are included in this work) for the evaporated and PECVD films respectively after annealing for various times, while \( I_{\text{max}} \) and \( I_{\text{max}} \) are the relevant intensities for the films after full crystallisation over 24 hrs.
Figure 6: XRD patterns of EVA and PECVD \((H^+ \quad \text{and} \quad H^-)\) films after annealing for 8 hrs, with three major diffraction peaks of Miller indices; and the definition of the Normalised Cristal Quality factor of XRD \((Q_{xrd})\) for the films.

\[ Q_{xrd} = \frac{I_{(111)} - I_{(100)}}{I_{(100)}} \times 100\% \]

\( I_{(111)} \) and \( I_{(100)} \) are intensities of the \((111)\) and \((100)\) peaks, respectively.

\( Q_{xrd} \) of the evaporated and PECVD films is shown in Fig. 7 as a function of the annealing time. It increases more rapidly for the evaporated films compared to the PECVD (both \(H^+\) and \(H^-\)) films for the times between 5 and 10 hrs, and then it develops similarly for both film types, strongly in agreement with the results of the UV-reflectance measurements.

Figure 7: Normalised Cristal Quality factor of X-ray diffraction \((Q_{xrd})\) of EVA and PECVD \((H^+ \quad \text{and} \quad H^-)\) films as a function of annealing time.

Raman spectroscopy is a fast, non-destructive, and convenient diagnostic tool for characterising the structural properties of thin-film [11]. Fig. 8 shows the Raman spectra of the evaporated and PECVD \((H^+ \quad \text{and} \quad H^-)\) films after annealing for 6 hrs \((c\text{-Si as reference})\), with inset values of the Raman peak centre and the full width at half maximum (FWHM). Note that the laser beam probing area is small, about 5µm in diameter, so the values of Raman peak centre and FWHM are averaged for nine different positions taken over the area of \(25 \times 25 \mu m^2\).

The Raman peak centre and its FWHM for the evaporated films change faster than those for the PECVD films (both \(H^+\) and \(H^-\)) films in the direction of the respective value for \(c\text{-Si}\) as a reference, with inset values of the Raman peak centre and the full width at half maximum (FWHM). Note that the laser beam probing area is small, about 5µm in diameter, so the values of Raman peak centre and FWHM are averaged for nine different positions taken over the area of \(25 \times 25 \mu m^2\).

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SEM images of the evaporated and \(H^+\) PECVD after SPC for 24 hrs followed by Secco etching are shown in Fig. 10. It can be seen that more grain boundaries present in the \(H^-\) PECVD film than in the evaporated film. The average grain size estimated from the images is larger in the evaporated film than in the PECVD film, or 2.3 and 1.5 µm respectively.

4 DISCUSSIONS

Four characterisation methods (OTM, UV-R, XRD and Raman) indicate that the crystal growth starts after about 4 hours at 600°C, perhaps, marginally earlier in the evaporated films, and its intermediate stage, where the crystallisation degree quickly increases from 5% to 70%, has a higher rate in the evaporated films than in both \(H^+\) and \(H^-\) PECVD films. About the same onset of the crystallisation points at similar incubation and nucleation times/rates in all films regardless the presence of hydrogen.
The OTM images have an evidence of more sparse nuclei in the EVA films and PECVD films, but all four methods (OTM, UV-R, XRD and Raman) agree that those sparse nuclei are more active and develop into faster growing grains. The SEM images after Secco etching reveal that the average grain size in the evaporated films is slightly larger than that in the H-PECVD films. Therefore, the resulting quality of evaporated poly-Si diodes should be at least as good as for the PECVD poly-Si diodes, which have demonstrated the cell efficiency of 10.4%. The faster crystal growth in the evaporated films potentially allows a shorter SPC process for poly-Si thin-film cell fabrication.

5 SUMMARY

Four independent film characterisation methods (OTM, UV-R, XRD and Raman) produced the evidence that for the SPC process at 600°C the evaporated films have similar incubation and nucleation times as the PECVD films but the number of initial crystal grains is less and their growth rate is faster in the evaporated films, which makes a shorter SPC process feasible. SEM images also reveal that the resulting quality of poly-Si diodes made by evaporation should be at least as good as for those made by PECVD promising similar cell efficiencies. Hydrogen is not responsible for the observed differences between SPC of the films from two different deposition methods.

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