Diode laser crystallization processes of Si thin-film solar cells on glass

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Abstract The crystallization of Si thin-film on glass using continuous-wave diode laser is performed. The effect of various processing parameters including laser power density and scanning speed is investigated in respect to microstructure and crystallographic orientation. Optimal laser power as per scanning speed is required in order to completely melt the entire Si film. When scan speed of 15–100 cm/min is used, large linear grains are formed along the laser scan direction. Laser scan speed over 100 cm/min forms relatively smaller grains that are tilted away from the scan direction. Two diode model fitting of $S_{uns}-V_{oc}$ results have shown that solar cells crystallized with scan speed over 100 cm/min are limited by grain boundary recombination ($n = 2$). EBSD micrograph shows that the most dominant misorientation angle is 60° . Also, there were regions containing high density of twin boundaries up to $\sim 1.2 \times 10^{-8}/\text{cm}^2$. SiO_x capping layer is found to be effective for reducing the required laser power density, as well as changing preferred orientation of the film from $\langle 110 \rangle$ to $\langle 100 \rangle$ in surface normal direction. Cracks are always formed during the crystallization process and found to be reducing solar cell performance significantly.

1 Introduction

Polycrystalline silicon thin-film solar cells on glass are strong candidate for next generation photovoltaic technology as it combines advantages of both wafer Si solar cells technology and thin-film solar cells technology. Si material has advantages of nontoxicity and low-cost. Commercial polycrystalline silicon thin-film solar cells have been fabricated by CSG Solar which achieved photovoltaic conversion efficiency of 10.4% in 2007 [1]. In this solar cell, 2 μm thick a-Si thin-films on borosilicate glass were crystallized using solid phase crystallization (SPC) process which produced grain sizes in the range of 1–2 μm . However, high density of intragrain defects are generated during the SPC process and it was found to be lifetime limiting recombination pathway which greatly limit the open-circuit voltage [2]. Alternate to SPC, it was reported that continuous-wave (CW) diode laser crystallization of Si thin-film on glass can form defect-free grains with very large grains size up to few tenths of millimeters in length [3]. Performance potential of this solar cells has shown that photovoltaic conversion efficiency above 13% can be achieved with a diffused homo-junction emitter [4].

In this work, the diode laser crystallization processes of Si thin-film on glass are reported in detail. Grain microstructure and crystallographic orientation were investigated in terms of the laser parameters. Then, effect of SiO_x capping layer is investigated in terms of the crystallization parameters and crystal orientation. Finally, cracks in the film are discussed and their influence on solar cell performance is evaluated.

2 Experiment

On a 3.3 mm thick planar borosilicate glass (Schott Borofloat33) with an area of $50 \times 50 \text{ mm}$, SiO_x 100 nm thick barrier layer was deposited by plasma-enhanced chemical vapor deposition (PECVD) at 200–300 $^\circ\text{C}$, below 1 mT at deposition rates of 5–30 nm/min. Then, the SiO_x layer was subjected to a dehydrogenation annealing step at 500 $^\circ\text{C}$ for 2 h under N_2 flow. 10 μm thick Si films were deposited by e-beam evaporation at 350–650 $^\circ\text{C}$. During the deposition, in-situ boron doping was performed to realize a boron concentration of $\sim 5 \times 10^{15}$ to $\sim 2 \times 10^{16} \text{ cm}^{-3}$. The Si films were placed on pre-heated stage at 650 $^\circ\text{C}$ for 3 min. Subsequently, CW diode laser (FWHM, 0.17 cm wide and 12 cm long) was scanned perpendicular to the 5 cm long axis for crystallization. After

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Fig. 1. (Left) Optical microscope image and (right) TEM image of diode laser crystallized Si film (40 cm/min with 15 kW/cm²) with complete melting of entire film.

Fig. 2. (Left) Optical microscope image and (right) TEM image of diode laser crystallized Si film (40 cm/min with 9.7 kW/cm²) with partial melting of film.

removal of native oxide formed during the crystallization by HF dip, phosphorous dopant source (P508, Filmtronics, Inc.) was spin-coated. Subsequently, rapid thermal process (RTP) was conducted at 870 °C for 2 min. Junction depth around 500 nm was achieved and emitter sheet resistance of 300–500 ohms/□ was obtained. The hydrogen passivation was applied through remote plasma passivation at ~650 °C for 20 min. Point contact metallization method is applied as described in reference [5].

The crystallographic orientation was analyzed by X-ray diffraction (XRD). Philips X'Pert MRD 4-circle diffractometer using Cu-K_α radiation. Receiving slit of 7 mm² was used and (100), (110), (111), and (422) pole figures were measured with background subtraction. Samples were placed in the center of an open three axes goniometer in Bragg orientation up to 75° tilting angle. Measurement time per step was between 5 and 10 s, step size for both rotation and tilting was 5°. The data was corrected and analyzed using X'pert Texture (Version 1.1a) software which can generate pole figures and inverse pole figure maps. For high resolution electron beam scattering diffractometer (EBSD) measurement, a NordlysF detector EBSD analytical system interfaced to a Carl Zeiss AURIGA® CrossBeam® workstation was used.

3 Results and discussion

3.1 Liquid phase crystallization of Si film

Figures 1 and 2 are showing two distinctly different microstructures after Secco etching and the corresponding

TEM images of the laser crystallized Si thin-films. In our diode laser system, laser scan speed (cm/min) and power density (W/cm²) are two major parameters that control the crystallization process. Appropriate laser power density is required to completely melt the entire film [3]. Figure 1 represents the desired microstructure with large linear grains grown parallel to the laser scan direction when scan speed of 40 cm/min with laser power density of 15 kW/cm² is used. Corresponding TEM image shows defect-free grains that were formed by complete melting of the film. Grain size can be up to few tenths of millimeters in length and several nanometers to several hundred microns in width. On the other hand, if the power density is insufficient to melt the entire film, only surface melting occurs and generates columnar grains several microns in size as shown in Figure 2. In this case, scan speed of 40 cm/min with laser power density of 9.7 kW/cm² is used. Corresponding TEM image of partially melted Si film shows the formation of columnar grains at the surface which extends few microns into the film. If the power density is higher than the required power to achieve full-melting, film delamination takes place.

Figure 3 is EBSD micrographs and corresponding misorientation charts of the completely melted films that were scanned at 40 cm/min at 15 kW/cm². Due to the top-hat profile of the laser beam, intensity at the edges of the laser traces is not sufficient to achieve full-melting and form small columnar grains as shown in Figure 3a. The corresponding misorientation chart is showing that there are variety misorientation angles with relatively higher number of 60° misorientation. As the intensity of the beam

Fig. 3. EBSD micrographs and corresponding charts showing the relative frequency corresponding to each misorientation value of the laser crystallized films (40 cm/min with 15 kW/cm²) showing (a) small columnar grains at left edge; (b) parallel grains meet each other; and (c) twin boundaries. Note that red lines represent twin boundaries.

gets stronger towards the middle region, the melt depth increases and the film becomes liquid phase. As the laser scans, this liquid Si solidifies along with, it forming large linear grains along the scan direction. Figure 3b is showing termination of growth of such linear grains when adjacent grains meet each other. If the grains do not converge, they can grow continuously until the scan stops. Such parallel

grains have 60° misorientation angles which are marked in red lines. Frequently, there are regions where high density of parallel grain boundaries, up to $\sim 1.2 \times 10^{-8}/\text{cm}^2$, are formed, as shown in Figure 3c. All of these boundaries are found to be 60° misorientation as shown in corresponding relative misorientation chart and large number of these boundaries are found to be first order $\Sigma 3$ twin boundaries.

Fig. 4. Required laser power density to achieve full-melting of Si film vs. laser scan speed with and without capping layer.

3.2 Effect of SiO_x capping layer

In laser processing of Si film, few hundred nanometers thick SiO_x capping layer is often deposited on top of the Si film in order to enlarge grain size of the film [6]. When 100 nm thick SiO_x capping layer is deposited by PECVD, the required power density for full-melting of the film is reduced due to an antireflection effect. Figure 4 is an empirically obtained graph showing the required laser power density to achieve full-melting as a function of scan speed with and without capping. As can be seen from this graph, the required power density is lower when the capping layer is used. This can be explained by an antireflection characteristic of the SiO₂ layer which enhances the absorption of the laser power. Our measurement shows that absorption at 808 nm is increased from 56% to 65%. In addition to the enhanced absorption, the capping layer stores some of generated heat during the laser irradiation and the heat flows back into the Si film which elevates temperature of the film [7].

Pole figure measurements are performed using XRD and Figure 5 is showing *x* (surface normal), *y* (scan direction), and *z* (plane normal) inverse pole figure maps of completely melt Si film with and without the capping layer. As can be seen, when there is no capping layer, (110) preferential orientation in *z* direction is present. Also, there is a maximum intensity present at (112) orientation for both *x* and *y* directions. Although this type of orientations is not uniformly distributed all over the crystallized area, it is a very common crystallographic orientation distribution in our film. When the capping layer is applied, (100) preferential orientation is found in *z* direction. Highest intensity at (110) orientation is formed along the *x* direction while highest intensity is found at (111) orientation in *y* direction. According to Atwater et al. [8], the interfacial energy at the interface between SiO₂ intermediate layer and Si film determines the (100), (110), and (111) preferential orientation in plane normal of the Si film. The interfacial energy depends on heat flow

Fig. 5. Inverse pole figure maps of completely melt Si film at scan speed of 80 cm/min with and without the capping layer.

Fig. 6. Sheet resistance as function of scan speed.

during crystallization process and (100) orientation requires longest melt duration [9]. As mentioned earlier, the capping layer elevates temperature of the film and thereby it has effect of extending duration of liquid state. As a result, the (100) preferred orientation formation could have been allowed by extended melt duration in our case.

3.3 Effect of laser scan speed

Figure 6 is a graph of sheet resistance as function laser scan speed. The sheet resistance is almost comparable for the scan speed between 15–80 cm/min. However, the sheet resistance starts to increase from 80 cm/min and further more rapidly from 100 cm/min. Microstructure of the laser crystallized films scanned at 40 cm/min and 160 cm/min is shown in Figure 7. As can be seen, grains are severely tilted away from the scan direction when 160 cm/min is used. Figure 7 is a schematic illustration of these two grain growth behaviors. Zone 1 is liquid phase and Zone 2 is a phase transition region where liquid Si is in cooling stage. Zone 3 refers to a solid phase region with very high surface temperature. As can be seen, area of the Zone 2 is much larger in Type I compared to Type II. Due to excessively

Fig. 7. Schematic illustration of grain growth behavior on two distinct scan speed regimes. Type I refers to scan speed of 15–100 cm/min and Type II refers to scan speed over 100 cm/min.

fast scan speed in Type II, temperature in this region decreases rapidly. Therefore, molten Si quickly transforms into solid phase. As a result, grain growth cannot follow the scan direction and thus forms in random directions. Whereas, Type I provides long enough time for grain formation thereby grain growth can proceed along the scan direction.

Emitter was formed on these two types of microstructures and $Suns-V_{oc}$ was measured after removing some portion of emitter to make contact with the absorber. Figure 8a is showing the obtained data and fitted curve of solar cells that were crystallized at scan speed of 40 cm/min with 15 kW/cm². $Suns-V_{oc}$ curves are useful to identify diode properties such as open-circuit voltage, pseudo fill factor, diode ideality factors, etc., and to determine the effects of bulk and depletion region recombination [10]. Obtained data is fitted to two-diode model ($n = 1$ and $n = 2$) in order to obtain parameters V_{oc} , V_1 , V_2 and R_{sh} . Detailed fitting analysis is described in elsewhere [11]. Two characteristic voltages V_1 and V_2 are obtained at the intersection of the two fitted curves for the $n = 1$ and $n = 2$ diodes correspondingly with the horizontal line at 1-Sun light intensity. Generally, the $n = 2$ diode ($V_1 > V_2$) accounts for SRH (Shockley-Read-Hall) recombination in the junction space charge region and at grain boundaries, whereas the $n = 1$ diode ($V_1 < V_2$) accounts for bulk and surface recombination.

As depicted in Figure 8b, 1 and 0.1 $Suns-V_{oc}$ were 525.9 mV and 445.9 mV for the laser crystallized solar cells at 40 cm/min and 160 cm/min, respectively. It is also shown that $n = 1$ recombination ($V_1 < V_2$) is dominant for the 40 cm/min sample, while $n = 2$ recombination ($V_1 > V_2$) is dominant for the 160 cm/min sample. Presumably, the grain boundaries tilted away from scan direction formed in 160 cm/min act as a carrier recombination center and limits the solar cell performance.

(a)

(b)

Fig. 8. (a) $Suns-V_{oc}$ measurement of the laser crystallized solar cells (40 cm/min with 15476 W/cm²) with fitted curve. (b) $Suns-V_{oc}$ results of scan speed of 40 and 160 cm/min.

3.4 Solar cell performance and effects of film cracks

It is clear that large cracks, width up to several hundred microns and length up to several millimeters are generated along the scan direction as shown in Figure 9. The position of the crack formation is random. In some case, few centimeters long cracks could be generated in right middle or near to the edges of the crystallized area. The cracks are always generated during the laser crystallization process and likely responsible for shunting problem when $p-n$ junction is formed and metallized. It is shown that grain boundaries continue even after the crack which implies that the crack occurred after the film is solidified. Also, structural defects are often observed near the crack which is not surprising since the crack is likely to be formed by excessive tensile stress in the film. The stress could be responsible from high undercooling rate as well as the spatial non-uniformity of the undercooling rate. Solar cell device is fabricated on absorber layer crystallized at scan speed of 80 cm/min by RTA emitter diffusion. After hydrogen passivation, the material is metallized using the point contacts. Figure 10 compares two types of cells, one with few severe cracks running through the middle of entire active area of the cells and one that the active area is made in the region of no crack. As can be seen, shunt resistance of the cell without cracks is around two times higher for the cell with cracks. Also, V_{oc} and J_{sc} , and FF

Fig. 9. (Left) SEM image of cracked region and (right) real image of cracks.

Fig. 10. Light I - V curve comparison of solar cells with cracks and without cracks.

are lower for the cell with cracks. Overall efficiency is also reduced from 7.1% to 5.9% due to the cracks. Film cracking presents a major challenge for the laser crystallization of thin-film on glass.

4 Conclusions

High quality polycrystalline Si thin-film on glass was fabricated using CW diode laser crystallization. It was necessary to melt the entire silicon thin-film to obtain desired microstructure. When scanning speed was between 150 to 100 cm/min, large linear grains were formed, up to few tenths of millimeters in length and up to several hundred microns in width. Grain growth ceased when

adjacent grains meet. High density of parallel grain boundaries is present frequently which was found to be twin boundaries. SiO_x capping layer is found to be effective in reducing the required laser power density to achieve full-melting of the film. Also, preferred orientation is changed to (100) from (110) in surface normal direction when the capping layer is used. Two types of growth behaviors, Type I and Type II, are identified in respect to laser scan speed. In Type II (over 100 cm/min) growth behavior the solid and liquid phase region was shortened compared to that of Type I (15–100 cm/min). As a result, grains growth could not follow the scan direction and tilted away from the scan direction. $Suns-V_{oc}$ measurement showed that band to band recombination was dominant for Type I while grain boundary recombination was dominant for Type II. Cracks are generated during the laser crystallization and it was found to reduce solar cell efficiency from 7.1% to 5.9%.

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