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Crystallization and surface texturing of amorphous-Si induced by UV laser for photovoltaic application

Lei Hong, Xincai Wang, Rusli, Hao Wang, Hongyu Zheng et al.

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I. INTRODUCTION

Polycrystalline silicon (poly-Si) thin film has been actively studied for solar cell application due to cost reduction promise compared to crystalline bulk Si. Poly-Si film generally needs to be fabricated directly on cheap foreign substrates (glass or plastic), which poses a constraint to apply high temperature to better the film quality. Laser annealing is thus considered as an important approach to get high quality poly-Si without damaging the substrate. Traditionally, excimer lasers (typically 248/308 nm) are used due to their short wave-length, which can be easily absorbed by silicon. However, the operation and maintenance cost of excimer laser is high. It also requires a long processing time to accomplish a uniform crystallization on a large substrate, given that the repetition rate for excimer laser is normally limited to 300 Hz. Therefore an alternative efficient approach of using diode pumped solid state (DPSS) Nd:YVO4 UV laser is pursued. The crystallization mechanism is explained as follows: (i) There is a laser processing window where the power intensity of the optical beam is sufficient to melt the Si films and a stage of coexistence of solid and liquid regions can be sustained. (ii) the crystallization then follows the sequential lateral solidification (SLS) process in which generated Si crystal seed can be dragged epitaxially in the desired lateral direction, and (iii) further lateral growth of the previously formed grains via epitaxial growth could possibly be attained by properly adjusting the relative position between the sample and incident beam. Hence, after the repeated exposure to the laser beam, poly-Si film can be achieved.

In this paper, we report the laser induced crystallization based on the above mechanism and surface texturing on amorphous silicon (a-Si) in a one-step process with 355 nm DPSS Nd:YVO4 laser. The optimal laser annealing condition for crystallization and nano-dome structure formation of 400 nm thick silicon has been identified. The material quality and light trapping ability for the laser treated a-Si is found to be improved. The developed process has potential application in the fabrication of high efficiency thin film Si solar cell.
sample was translated by a distance of 1 \( \mu \)m between each laser pulse to facilitate the lateral crystalline growth. After each scan, the sample was moved in the y direction by a distance of 100 \( \mu \)m to get a beam overlap of \( \sim 97\% \). In order to find the optimum conditions, the laser scanning was conducted at various laser energy densities from 196 mJ/cm\(^2\) to 507 mJ/cm\(^2\). The morphologies of the laser treated samples were analyzed using field-emission scanning electron microscopy (FESEM, LEO, 1550 Gemini, resolution 1 nm), and atom force microscope (AFM, NS3 A). Raman spectra were recorded at room temperature with the excitation wavelength of 532 nm (WITec, alpha300 R, resolution 2 cm\(^{-1}\)). The reflection and transmission spectra were measured with Lambda 950 UV-VIS-NIR scanning spectrophotometer (PerkinElmer, resolution for UV/Visible light is 0.05 nm, for infrared light is 0.2 nm).

### III. RESULTS AND DISCUSSION

Figures 2(a)–2(e) depict the SEM images of the laser treated Si surfaces with different energy densities from 266 mJ/cm\(^2\) to 439 mJ/cm\(^2\). Figure 2(a) shows the untreated a-Si film with no surface modification. Figure 2(b) shows the surface profile with energy density of 231 mJ/cm\(^2\), below which...
the laser is not able to melt the a-Si film. In this case, minor surface modification and small grain of poly-crystalline are observed due to partial melting of the silicon film. For energy density of 294 mJ/cm², major surface morphology change is observed (Fig. 2(c)) compared with the as-deposited silicon film. When the energy density is increased to 380 mJ/cm², the film is crystallized and yields the nano-dome structure as shown in Fig. 2(d). At this energy density, the crystallization falls into solid liquid growth regime as modeled by Im. During the laser annealing, the a-Si film is almost completely melted with small solid islands at the interface of silicon and glass, acting as solidification seeds during cooling. Due to the temperature gradient between the solid and liquid silicon, it tends to lead to the hydrodynamic motion, which will instigate surface tension and capillary waves. Thus, the surface morphology is changed with the dome structure formed. Figure 3 presents the SEM image of laser treated silicon film after Secco etch irradiated under the optimal condition of energy density of 380 mJ/cm², repetition rate of 20 kHz and scanning speed of 20 mm/s. The etching solution is prepared with HF and K₂Cr₂O₇ concentration of 9.3 mol/L and 0.025 mol/L respectively. Due to the higher defect density of grain boundaries, they reacted much faster with Secco etchant. Consequently, the grain boundaries are clearly revealed by delineating those defects, indicating the good crystallization. Figure 2(e) illustrates that the continuous Si film breaks and shrinks into spherical beads, implying serious damage when increasing the energy density to 439 mJ/cm². This agglomeration is speculated to be caused by outburst of the heterogeneously nucleated vapor bubble inside the silicon layer. At this high pulse energy, the film is completely melted with vapor bubbles formed in the liquid film. Those bubbles then diffuse and burst at the outer surface, breaking the continuity of the film. Therefore, it indicates that the maximum energy density for crystallization is 439 mJ/cm².

Figure 4 shows the Raman spectra of a-Si thin films treated at different energy densities to study the crystalline property of the laser treated films. For the as-deposited sample, it exhibits a broad and weak peak at ~480 cm⁻¹, corresponding to the typical spectrum for a-Si. With increasing laser energy density from 294 to 507 mJ/cm², the peak of Raman spectrum shifts toward 520 cm⁻¹, suggesting the formation of crystalline silicon. The estimated crystalline volume fractions of the crystallized Si are calculated from the Raman spectra. When energy density is 294 mJ/cm², 64% of the film is crystallized. For the optimal energy density 380 mJ/cm², it produces ~98% crystalline volume fraction. Although further increase of the energy density can realize complete crystallization but the surface continuity is broken. At energy density of 507 mJ/cm², the spectral width is broadened and the peak is shifted backward to 515 cm⁻¹, which may be due to the ablation of the Si film as explained previously.

Not only is the a-Si film crystallized, but also it attains a nano-dome surface structure. Figure 5 demonstrates the surface profiles of the as-deposited and laser processed 400 nm a-Si thin film by the AFM measurement. It is observed that a regular nano-dome pattern is achieved after UV laser treatment with pulse energy of 380 mJ/cm². The diameter of the nano-dome structure is around 300 to 500 nm with a height of ~200 nm. The primary reason for surface texturing is due to the difference in densities between solid and liquid silicon. Since the liquid silicon is much denser than the solid silicon, as the solid region grows after melting, it tends to expand and produces ridges and hillocks around the grain boundary. More importantly, the previously produced nanostructure can act as a diffraction grating for the following laser beam illumination. Hence the generated diffracted waves along the surface interfere with the incident waves, modifying the surface morphology when the interference is sufficiently strong.
R and T spectra were measured by UV-VIS-NIR spectrophotometer, whereas the absorption spectra were obtained by 100-R-T %. For the as-deposited a-Si, reflection (with peak value around ~50%) and transmission (with peak value around ~85%) are high with strong oscillation for longer wavelength beyond 500 nm. Upon the scanning of the UV laser, the absorption increases with the reduction of the reflection and transmission for all different pulse energies. When the energy density is 294 mJ/cm², the absorption increment is obvious for the short wavelength light (<600 nm). The reflection drops from ~35% to ~20% for wavelength of 400 nm. With no change in the transmission, hence the absorption increases by 15%. Nevertheless, the improvement in long wavelength light region (>600 nm) is not evident. This is because at low laser energy, it is insufficient to induce crystallization and major surface modification for a-Si. The film remains amorphous and the feature size formed is much smaller than that of long wavelength light. The light fails to distinguish the structure and thus is relatively easy to penetrate through the film.18 When the energy density is increased to 380 mJ/cm², the nano-dome structure has a feature size compatible with 400 nm, which locates near the peak of solar spectrum. Hence, the interaction of the incident light with the structure is dominated by the scattering effect, which dramatically prolongs the optical path length of sunlight.19,20 Besides, the dome structure has a gradual change of the effective optical path length.
refractive index, which functions as a good antireflective coating. Furthermore, the point with occurrence of oscillation for reflection and transmission spectra shifts toward ~800 nm compared with ~500 nm of as deposited a-Si thin film and the absorption for the long wavelength (beyond 730 nm, corresponding to the bandgap of a-Si:1.7 eV) is effectively increased. This can be correlated with the band-gap variation after crystallization (band-gap changes to 1.1 eV for polycrystallized Si). As a result, the absorption enhancement (or ultimate efficiency, calculated by integrating the absorption efficiency variance due to the change of thickness) of 300/400 nm is irradiated by sunlight of wavelength from 300 nm to 1100 nm. The height of nanodome texturing. It is also observed that the absorption spectra are obtained after subtracting the reflection on the top surface and transmission on the bottom surface. The details of the construction of the structure can be found elsewhere. It is obvious that the experimental result is consistent with the simulation for wavelength ranging from 300 nm to 800 nm, especially for the periodicity of 400 nm, indicating good quality of laser processed nanodome texturing. It is also observed that the absorption spectrum of the simulated structure exhibits oscillation compared with the experimental result, which is due to the interferences among the perfect periodic structures.

IV. CONCLUSIONS

In conclusion, it was demonstrated that 355 nm DPSSL Nd:YVO4 laser successfully crystallized and textured the a-Si thin film in a one-step annealing process. With the energy density of 380 mJ/cm2, 98% of the 400 nm thick a-Si was converted to poly-Si with a crystallization depth of 400 nm and the nanodome texturing was formed of periodicity around 300 to 500 nm. The absorption enhancement over the whole standard AM 1.5 solar spectrum of the UV laser treated Si thin film was found to be increased by ~200% compared with original a-Si. The ultimate efficiency increased from 8.1% to 23.9% for wavelength ranging from 300 to 1100 nm. The improved material quality and enhanced light trapping capability make it very promising for the applications of high efficiency Si thin film solar cells.

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