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

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The DPSS Nd:YVO₄ UV laser is used to anneal amorphous silicon (a-Si) film to achieve crystallization and nano-dome surface texturing simultaneously in a one-step annealing process. With pulse energy of 380 mJ/cm² and repetition rate of 20 kHz, the a-Si can be crystallized by the sequential lateral solidification process, which is evidenced by both SEM characterization and Raman spectra. In addition, the nano-dome like structure is confirmed by AFM characterization, which can lead to ~200% boost in terms of light absorption as measured by UV-Visible - Near-infrared scanning spectrophotometer. This study highlights the great potential of Nd:YVO₄ UV laser for its application in thin film Si solar cell industry to improve the film quality and light trapping capability. © 2012 American Institute of Physics. [doi:10.1063/1.3686612]

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.¹ 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 wavelength, which can be easily absorbed by silicon.^{2,3} 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.⁴ Therefore an alternative efficient approach of using diode pumped solid state (DPSS) Nd:YVO₄ UV laser is pursued.⁴ 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,⁵ (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,^{6,7} 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.⁸ 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.

II. EXPERIMENTAL DETAILS

Figure 1 illustrates the schematic of the laser annealing process. The a-Si film with a thickness of 400 nm was deposited on the glass substrate (corning 1737, 25 × 25 mm²) with a SiO₂ buffer layer of thickness 100 nm (Fig. 1(a)) by plasma enhanced chemical vapor deposition (PECVD, Cello Aegis-20). SiH₄ was used for the deposition of silicon/SiO₂ operated at radio frequency (RF 13.56 MHz) with a deposition pressure 400 of mTorr. The RF powers used for the growth of SiO₂ and a-Si were 20 W and 60 W, respectively. In order to control the hydrogen desorption, the deposition was conducted at a high temperature of 400°C to obtain a hydrogen content of ~2 at.%, as measured by Fourier transform infrared spectroscopy (FTIR).

The Q-switched DPSS Nd:YVO₄ laser (Coherent Avia-X) was then used for the annealing process. The laser wavelength is 355 nm and the laser pulse frequency ranges from 1 kHz to 100 kHz. The pulse duration of the laser beam is 20 ns to 35 ns depending on the laser pulse frequency used. The output beam profile is Gaussian shape and the spatial mode is TEM₀₀ (M₂ < 1.3). The beam divergence is less than 0.3 mrad. During the crystallization, the laser beam with a diameter of 3.5 mm (@ 1/e²) was focused by a cylindrical lens with a focal length of 100 mm so as to obtain a line shape beam with a width of 50 μm. The crystallization was performed in air at room temperature. The position of the laser beam was fixed and a computer-controlled X-Y translation stage (with accuracy of 5 μm) was used to move the sample in the x direction with a constant scanning speed of 20 mm/s. The repetition rate was set at 20 kHz. Accordingly, the

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FIG. 1. (Color online) Schematic illustration of laser crystallization process on a-Si thin film: (a) As-deposited 400 nm a-Si on 100 nm SiO₂ coated glass surface; (b) laser annealing of a-Si thin film; (c) nanodome structure formation after laser annealing; and (d) Secco etch to reveal the grain boundaries.

sample was translated by a distance of 1 μm between each laser pulse to facilitate the lateral crystalline growth.⁴ After each scan, the sample was moved in the y direction by a distance of 100 μm 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

FIG. 2. SEM images of (a) as-deposited a-Si and 400 nm thick a-Si thin films irradiated under different laser energy densities, (b) 266 mJ/cm^2 , (d) 294 mJ/cm^2 , (e) 380 mJ/cm^2 , (f) 439 mJ/cm^2 .

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.⁹ 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.^{6,7,9} 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 etch¹⁰ 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.¹¹ 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,

FIG. 3. SEM image of a-Si film irradiated under the optimal laser condition of energy density of 380 mJ/cm², repetition rate of 20 kHz and scanning speed of 20 mm/s after Secco etch.

FIG. 4. (Color online) Raman spectra of 400 nm thick a-Si thin films irradiated with laser energy densities: 294 mJ/cm², 380 mJ/cm², 439 mJ/cm², and 507 mJ/cm² with intensity peak around 520 cm⁻¹. The inset shows the Raman spectrum of the original as-deposited a-Si film, with the peak at ~480 cm⁻¹.

it exhibits a broad and weak peak at ~480 cm⁻¹, corresponding to the typical spectrum for a-Si.¹² 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.¹³ The estimated crystalline volume fractions of the crystallized Si are calculated from the Raman spectra.¹⁴ 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.^{15,16} 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,^{15,17} modifying the surface morphology when the interference is sufficiently strong.

Figure 6 depicts the reflection (R), transmission (T) and absorption (A) spectra for the as-grown and laser treated 400 nm thick a-Si thin films treated with energy densities of 294 mJ/cm², 380 mJ/cm², 439 mJ/cm², and 507 mJ/cm². The

FIG. 5. (Color online) Surface morphologies of (a) original as-deposited planar 400 nm thick a-Si thin film with a roughness of 3.4 nm and (b) UV laser irradiated film with laser energy density 380 mJ/cm². The AFM scan area is 5 $\mu\text{m} \times 5 \mu\text{m}$.

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 $\sim 50\%$) and transmission (with peak value around $\sim 85\%$) 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 $\sim 35\%$ to $\sim 20\%$ 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

FIG. 6. (Color online) (a) Reflection, (b) transmission, and (c) absorption spectra of laser treated 400 nm thick a-Si thin films with laser energy densities of 294 mJ/cm², 380 mJ/cm², 439 mJ/cm², and 507 mJ/cm². (d) Absorption spectra of the a-Si thin film with thickness of 100 nm. The original as-deposited planar 400 nm a-Si is used as a reference.

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,^{18,21} calculated by integrating the absorption efficiency over spectral irradiance of the standard AM1.5 G solar spectrum ranging from 300 to 1100 nm) improves by $\sim 200\%$ compared with as-deposited a-Si film and the ultimate efficiency increase from 8.1% to 23.9%. However, a further increase of the energy density to 439 mJ/cm² aggravates both the reflection for wavelength beyond 700 nm and transmission of short wavelength light below 600 nm. Together with the disappearing of oscillation phenomenon, it might be correlated with the fact that there is no complete film on the substrate due to agglomeration. Furthermore, the sensitivity of the layer thickness is investigated by reducing the film to 100 nm as shown in Fig. 6(d). It demonstrates that the absorption efficiency variance due to the change of thickness is negligible (the peak value of absorption drops from $\sim 90\%$ to $\sim 83\%$), providing additional flexibility for the process parameters. In summary, the laser treated film with pulse energy of 380 mJ/cm² yields a significant improvement in the optical absorption due to the nano-dome structure and bandgap change after crystallization.

Additionally, the experimental result is compared with simulation as shown in Fig. 7. For the numerical simulation, finite element method is used to solve the Maxwell's equation to model the laser induced structure. A unit dome cell bounded by periodical and perfect match layer with periodicity of 300/400 nm is irradiated by sunlight of wavelength ranging from 300 nm to 1100 nm. The height of nanodome

is 300 nm and the underlying silicon film is 100 nm. 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.²¹ 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 periodical structures.

IV. CONCLUSIONS

In conclusion, it was demonstrated that 355 nm DPSS 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 $\sim 200\%$ 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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FIG. 7. (Color online) Absorption spectra of (i) experimental 400 nm thick a-Si thin film irradiated with laser pulse energy 380 mJ/cm² and (ii) simulated Si nanodome structure with a periodicity of 300 nm and 400 nm. The dome height is 300 nm and the underlying film is 100 nm. The inset gives the simulated periodical nanodome structure.

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