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Leading Wave Crystallization from Fast Moving Molten Zone Formed by Micro-Thermal-Plasma-Jet Irradiation to Amorphous Silicon Films

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1. Introduction

In the fabrication of large-area electronics devices such as solar cells and thin-film transistors (TFTs), the crystallization of amorphous silicon (a-Si) films on glass substrates is one of the key process technologies. Various crystallization technologies have been extensively studied to form high-crystallinity Si films.[1-10] To improve the devices performance and uniformity, grain growth mechanism during rapid-thermal-annealing (RTA) and the control of grain structures including location and orientation have been investigated. In order to observe phase transformation of Si films, various measurement techniques have been proposed.[5-10] Transient reflectance measurements during RTA enable to observe phase transformation of Si film since molten Si has much higher reflectivity than that of solid Si.[5-7, 9, 10] Transient conductance measurement enables to obtain the volume of molten Si and liquid-solid interface velocity.[5-8] It is clarified that extremely fast movement of thin liquid layer and resulting fine grain crystalline formation, so called "explosive crystallization (EC)" takes place when pulsed-laser irradiation of a-Si is performed under partially melted condition.[8] Very high speed grain growth of the order several m/s is triggered by the release of latent heat at the liquid-solid interface, and double layer structure is observed from Si film after EC.[8, 9]

We have proposed the application of an atmospheric pressure DC arc discharge micro-thermal-plasma-jet (μ-TPJ) to high speed lateral crystallization (HSLC) of amorphous Si (a-Si) films on quartz.[11] In our previous study of HSLC-Si films, we attempted to melt Si films and move the molten region at a very high speed to induce a lateral temperature gradient and long range grain growth in a specific direction. *In-situ* transient reflectivity measurement during μ-TPJ irradiation suggested that solid phase crystallization (SPC) took place prior to the melting of Si film, and then molten region was generated within millseconds. In this study, we introduce microseconds time resolving high-speed-camera (HSC) for direct observation of phase transformation to better understand the crystallization mechanism from fast moving molten Si.

2. Experimental Procedure

Amorphous Si films were formed on quartz substrate by PECVD using SiH_4 and H_2 at 250 °C. Thickness of a-Si films was varied from 50 to 500 nm. Dehydrogenation was carried out at 450 °C in N_2 ambient for 1 hour. Schematic diagram of the μ-TPJ irradiation to a-Si films is shown in Fig.1. μ-TPJ was generated by DC arc discharge under atmospheric pressure with supplying power (P) of 0.8 ~ 1.7 kW. Ar gas flow rate (f) was varied from 1.0 to 4.2 L/min. The substrate was linearly moved by a motion stage in front of the μ-TPJ with scanning speed (v) ranging from 500 to 2000 mm/s. The distance between the plasma source and substrate (d) was varied from 1.0 to 1.5 mm. For the *in-situ* observation of grain growth of a-Si films during μ-TPJ irradiation, an optical microscope and a HSC were set on the motion stage on the backside of the substrate. The frame-rate (R_f) was varied from 3000 to 165000 frames per second (fps).

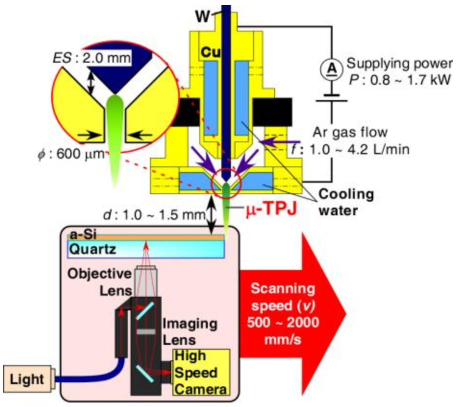

Fig. 1. Schematic diagram of the μ-TPJ irradiation to a-Si films.

3. Results and Discussion

Phase transformation of 100-nm-thick Si film during μ-TPJ irradiation was very clearly observed as a snapshot is shown in Fig. 2. The moving images were taken at very high-time-resolution of R_f = 16000 fps. We have succeeded in direct observation of grain growth from moving molten Si in millisecond annealing. Because liquid Si shows very high reflectivity due to free carrier, the molten region (MR) was seen in black as surrounded by red dotted lines in Fig. 2. SPC region formed in front of molten Si was clearly distinguished from amorphous phase. These results correspond with results of transient reflectivity measurement during μ-TPJ irradiation in our previous work.[11] Length and width of MR were 374 μm and 164 μm, respectively, and MR shape shows tendency to expand into scanning direction

Fig. 2. HSC image of Si film was shown during μ-TPJ irradiation to 100-nm- thick a-Si films under condition of P = 1.1 kW, d = 1.5 mm, f = 2.8 L/min, and v = 800 mm/s.

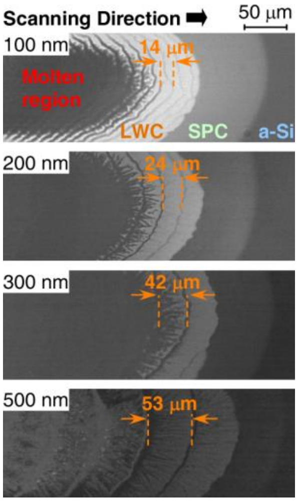

Fig. 3. HSC images Si film during μ-TPJ irradiation to 100 ~ 500 nm-thick a-Si films.

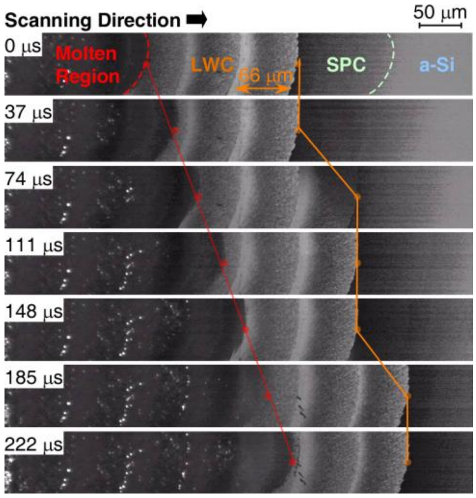

Fig. 4. HSC images of Si film taken at R_f = 27000 fps during μ-TPJ irradiation to 500-nm-thick a-Si films.

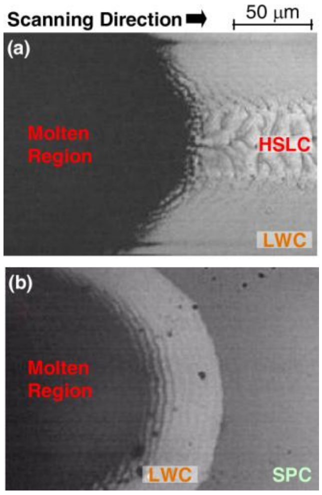

Fig. 5. HSC images of Si film during μ-TPJ irradiation under HSLC condition to (a) HSLC and (b) SPC -Si films.

with increasing *v*. Following the movement of MR, grains grew vertically to liquid-solid interface. It should be noted that there exist a region showing wave like pattern in between MR and SPC region. The obviously different contrast and pattern suggested completely unknown crystallization mechanism. We call this "Leading Wave Crystallization (LWC)" because its periodic and repeating structure are like waves.

To investigate LWC generation mechanism in order to better understand the behavior of LWC, HSC images during μ-TPJ irradiation to 100 ~ 500-nm-thick Si films were taken (Fig. 3). With the increase of thickness, the length of LWC wave increased from 14 μm and reached 53 μm in 500-nm-thick Si film. Latent heat are produced by difference of enthalpy during phase transformation, and the released latent heat at the growing front linearly increases with film thickness.[13] Therefore, the increase of LWC wave width with the increase of thickness suggests that not only heat conducted from μ-TPJ but also latent heat play a very important role in LWC generation. HSC images during μ-TPJ irradiation to 500-nm-thick Si film taken at a very high R_f of 27000 fps are shown in Fig. 4. MR moves at a constant speed, which is identical to the scan speed *v* of 650 mm/s. On the contrary, LWC front remained at a same position during 0 ~ 37 μs, then suddenly propagated ~ 66 μm ahead at 74 μs. Again, LWC did not occur during 74 ~ 148 μs, and explosive grain growth was occurred between 148 and 185 μs again. From higher time-resolved observation of R_f = 165000 fps, LWC propagation velocity was measured as high as 4500 mm/s, which is significantly faster than *v*. These results insist that LWC is quite similar to EC.[8-10] Very high speed grain growth of the order m/s is triggered by the release of latent heat from SPC-Si, and intermittent propagation of growth front forms periodic structure after EC. However, previous reports claim that driving force of EC is the released latent heat at liquid-amorphous Si interface. In the present case, EC propagates into SPC region, which obviously has less latent heat. In order to confirm this, μ-TPJ irradiation was first performed to form SPC and HSLC regions, and 2nd irradiation was performed to the films during HSC observation. In HSLC-Si region, no formation of LWC region was observed as shown in Fig. 5 (a). On the other hand, we clearly observed LWC by 2nd μ-TPJ irradiation to SPC-Si film as shown in Fig. 5 (b). This result indicates that sufficient latent heat remains in SPC region and the melting point of SPC-Si is lower than that of crystalline Si, which presumably triggers formation of liquid layer, and extremely fast propagation of the layer into SPC region. This suggests that quite an amount of disordered structure or amorphous component remains in SPC region. In addition, LWC Si films showed crystalline volume fraction of 100 % from Raman scattering spectra. This result strongly suggests that LWC region is formed via liquid phase.

4. Conclusion

We have succeeded in direct observation of grain growth from molten Si during millisecond annealing. Oval shape MR following the SPC region was successfully observed and lateral grain growth was vertically induced to liquid and solid interface. Furthermore, LWC similar to EC was newly discovered after SPC. It is declared that EC was generated at SPC-Si films.

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