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Flash-Lamp-Induced Explosive Crystallization of Amorphous Films Leaving Behind Periodic Microstructures

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1. Introduction

Non-thermal equilibrium annealing techniques have attracted significant attentions as the methods of forming device-quality films by crystallizing precursor amorphous films on low-cost substrates [1-5]. Of those annealing techniques, flash lamp annealing (FLA) is of great advantage especially for forming photovoltaic crystalline films because of its millisecond-order annealing duration which enables us to sufficiently heat μm-order-thick amorphous films without the entire heating of substrates [4,5]. We have so far found that FLA can induce the explosive crystallization (EC) of amorphous silicon (a-Si) films, self-catalytic lateral crystallization driven by the release of latent heat [6]. The flash-lamp-induced EC sometimes leaves behind periodic microstructures inside and on the surface of polycrystalline Si (poly-Si) films formed [6]. The fundamental understanding of this curious EC is quite important to apply this technique to the production of photovoltaic materials. In this study, we have attempted the crystallization of amorphous germanium (a-Ge) films, instead of a-Si films, by FLA in order to know whether the particular EC can occur universally in extensive materials. The microstructures of flash-lamp-crystallized (FLC) polycrystalline Ge (poly-Ge) films have also been observed in detail for the understanding of crystallization mechanisms in Ge films.

2. Experimental Procedures

About 3-μm-thick a-Ge films were deposited on 20×20×0.7 mm^3-sized quartz glass substrates at an Ar flow rate of 30 sccm, at a pressure of ~1 Pa, and at a RF power of 200 W, with no intentional substrate heating. a-Ge films then received a shot of quasi-5-ms flash lamp irradiation, consisting of discrete sub-pulses with tunable frequencies of 1-10 kHz. This quasi-millisecond pulse leads to the formation of macroscopic stripe patterns, visible to necked eyes, on the surface of crystallized materials, by the spacing of which we can estimate lateral crystallization velocity [7,8]. No pre-heating was performed for Ge films during FLA. Crystallization and crystalline fraction of Ge films after FLA were evaluated by Raman spectroscopy. Detailed microstructures of poly-Ge films were characterized with scanning electron microscopy (SEM) images, cross-sectional transmission electron microscopy (TEM) images, and electron diffraction patterns.

3. Results and Discussion

Figure 1 shows the surface image of a FLC poly-Ge film after FLA at a sub-pulse emission frequency of 5 kHz. One can see interference color on the surface of the FLA Ge film, indicating the existence of microstructures on it. We can also observe macroscopic stripe patterns on the surface, from which a lateral crystallization velocity is estimated to be 5-6 m/s. Figure 2 shows the Raman spectra of Ge films before and after FLA. A broad peak at around 270 cm^{-1} is seen in the spectrum of a Ge film, originating from a-Ge, while a sharp peak at ~300 cm^{-1} appears after FLA, which clearly indicates the formation of poly-Ge. Figure 3 shows the surface SEM image of a crystalline Ge film. One can see microscopic periodic surface roughness along a lateral crystallization direction, and the interval of the periodic structure is 0.7-0.85 μm. Similar periodic

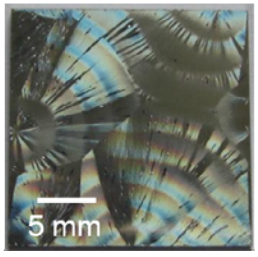

Fig. 1 Surface of a FLC poly-Ge film.

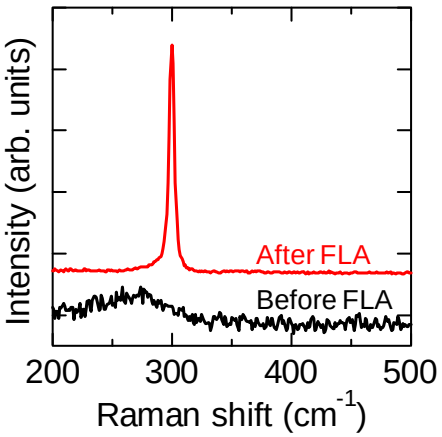

Fig. 2 Raman spectra of Ge films before and after FLA.

surface morphology can also be seen on the surface of FLC poly-Si, while the interval of the periodic structures is approximately 1 μm [6].

Figure 4 shows the cross-sectional TEM image of a FLC poly-Ge film. We can clearly see periodic structures also inside the poly-Ge film, in which two kinds of regions seem to appear alternatively along the crystallization direction. Electron diffraction patterns at the two characteristic regions are shown in Fig. 5. At a position (a), connecting to a concave surface part, multi-spot diffraction patterns are seen, which indicates the existence of multi-grains. On the other hand, at a position (b), which is in a region including a surface protrusion, only limited numbers of spots are seen in a diffraction pattern, meaning the formation of a larger grain.

All these features are quite similar to those of FLC poly-Si films formed from chemical-vapor-deposited or sputtered a-Si films [6,9,10], and EC may occur in the same manner. Grigoropoulos *et al*., have also reported similar periodic surface structure on the surface of poly-Ge films formed through laser-induced EC [12], and we probably observed the same phenomenon. Although they claimed that the formation of the periodic structures is due to solid-phase EC, the significant modulation of surface morphology and the existence of two regions having different characters, shown in Figs. 3 and 4, respectively, can never be explained by complete solid-phase process, and at least, partial melting process should be considered. Thus, we need more detailed considerations about the crystallization mechanisms of a-Ge films.

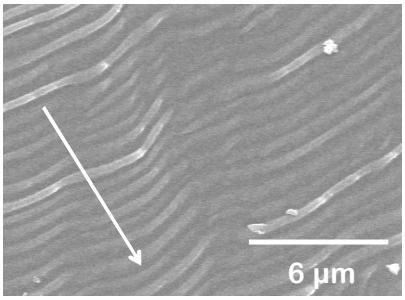

Fig. 3 Surface SEM image of a FLC poly-Ge film. An arrow indicates a lateral crystallization direction.

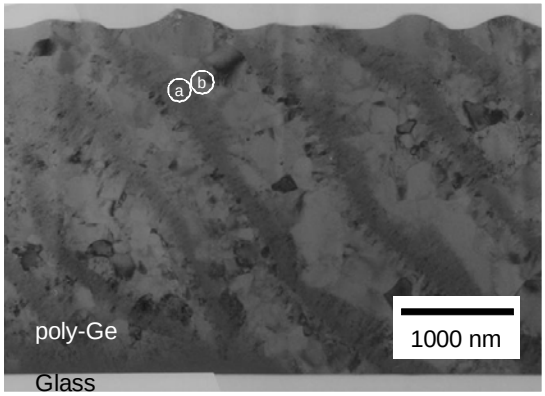

Fig. 4 Cross-sectional TEM image of a FLC poly-Ge film. The cross-section was formed along a crystallization direction.

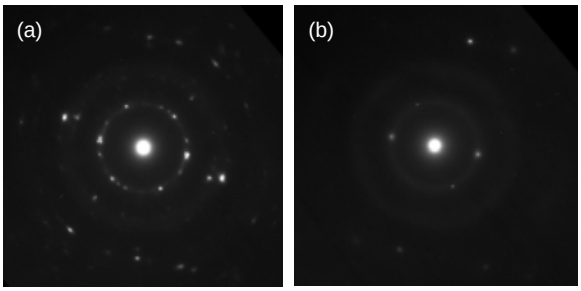

Fig. 5 Electron diffraction patterns of FLC poly-Ge observed at positions (a) and (b) indicated in Fig. 4.

4. Summary

The EC of a-Ge films can leave behind periodic surface microstructures, similar to the case of the EC of a-Si films. Microstructures inside poly-Ge films are also quite similar to those of FLC poly-Si, which may indicate the emergence of EC in the same crystallization manner. These facts mean that this curious crystallization could occur universally in a variety of materials.

Acknowledgements

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