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Description	

Polycrystalline Si films with unique microstructures formed from amorphous Si films by non-thermal equilibrium flash lamp annealing

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Flash lamp annealing (FLA), with millisecond-order duration, can crystallize amorphous silicon (a-Si) films a few μm thick on glass substrates, resulting in formation of polycrystalline Si (poly-Si) films with unprecedented periodic microstructures. The characteristic microstructure, formed spontaneously during crystallization, consists of large-grain regions, containing relatively large grains more than 100 nm in size, and fine-grain regions, including only 10-nm-sized fine grains. The microstructures results from explosive crystallization (EC), driven by heat generation corresponding to the difference of the enthalpies of meta-stable a-Si and stable crystalline Si (c-Si) states, which realizes lateral crystallization velocity on the order of m/s. The lateral crystallization may stop when the temperature of a-Si in the vicinity of c-Si, which is decided by both homogeneous heating from flash irradiation and thermal diffusion from c-Si, falls below a crystallization temperature. This idea is supported by the experimental fact that a lateral crystallization length decreases with decreasing pulse duration.

1 Introduction Thin-film polycrystalline silicon (poly-Si) is one of the candidates for high-efficiency and low-cost solar cell material because of the low amount of Si usage, long minority carrier lifetime, and high stability against light soaking. CSG solar AG has succeeded in the fabrication of solar cells with more than 10% efficiency using poly-Si films formed through solid-phase crystallization (SPC) of precursor amorphous Si (a-Si) films [1], demonstrating the availability of thin-film poly-Si solar cells. Their process is, however, based on long-time furnace annealing, resulting in low throughput. Although other approaches have been proposed [2-4], high-temperature processes up to 1000 °C preclude the possibility of using low-cost, conventional soda lime glass substrates. For the crystallization of a-Si films on glass substrates keeping glass temperature sufficiently low, non-thermal equilibrium treatment must be applied.

Flash lamp annealing (FLA) is an annealing technique with millisecond-order pulse light [5-7]. This annealing duration corresponds to the thermal diffusion length of glass and a-Si of approximately 50 μm, meaning sufficient heating of a-Si films a few μm thick, while avoiding thermal damage to glass substrates. We have actually demonstrated that poly-Si films more than 4 μm thick can be formed by FLA even on soda lime glass substrates [8, 9], and also succeeded in the operation of solar cells fabricated using the poly-Si films [10]. Furthermore, the crystallization of a-Si films by FLA is found to take place by a unique mechanism, unlike simple solid-phase or liquid-phase crystallization, resulting in the formation of unprecedented periodic microstructures. In this paper, we concentrate our attention on the unique periodic microstructures observed in the poly-Si films and their formation mechanisms.

2 Experimental details Cr adhesion films 200 nm thick were first formed by sputtering on quartz glass substrates 20×20 mm^2 in size, followed by the deposition of precursor a-Si films 4.5 μm thick by catalytic chemical vapor deposition (Cat-CVD). The Cat-CVD, often referred to as hot-wire CVD, can form a-Si films a few μm thick easily, unlike conventional plasma-enhanced CVD (PECVD), because of their low film stress. The detailed deposition conditions are summarized elsewhere [11].

Figure 1 shows the schematic diagram of a FLA system. Samples put on a holder receive flash irradiation from a Xe lamp array under Ar atmosphere. The sample holder was not pre-heated in this study. The flash lamp light has a broad spectrum mainly in visible range, which is therefore absorbed in a-Si films, resulting in increasing film temperature. The typical spectrum of the flash lamp light is seen elsewhere [7]. FLA was performed under pulse durations of 1 or 5 ms with various irradiances on the order of several tens of J/cm^2. No dehydrogenation process was performed prior to FLA. Only one shot of flash irradiation was supplied for each Si film.

The crystallization of Si films and their crystalline fraction were characterized by Raman spectroscopy. The 632.8 nm line of a He-Ne laser served as the excitation source. The surface morphology of the poly-Si films was observed by atomic force microscopy (AFM). The microstructures of inside poly-Si films were characterized by cross-sectional transmission electron microscopy (TEM).
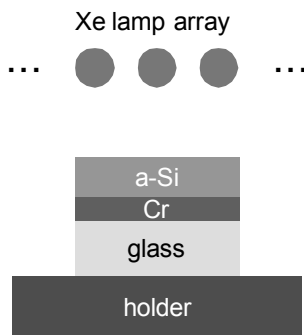

Figure 1 Schematic diagram of a FLA system. Flash irradiation was supplied under Ar atmosphere.

3 Results Figure 2 shows the surface images of the Si films after FLA with pulse durations of 1 and 5 ms under irradiances at which crystallized areas reach maximum without the peeling of the Si films. Only the edge parts are crystallized in the Si film after 1 ms pulse irradiation, while the whole Si film is crystallized after 5 ms irradiation. This means that crystallization tends to start from the Si film edges and expands toward center. According to the pulse durations and crystallization lengths, the crystallization velocity is estimated to be as high as more than 1 m/s. The result also indicates that the pulse duration of flash irradiation affects lateral crystallization length.
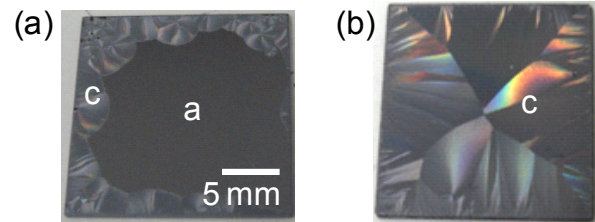

Figure 2 Surface images of Si films after FLA under (a) 1 ms and (b) 5 ms lamp irradiation. "a" and "c" indicate amorphous and crystallized parts, respectively.
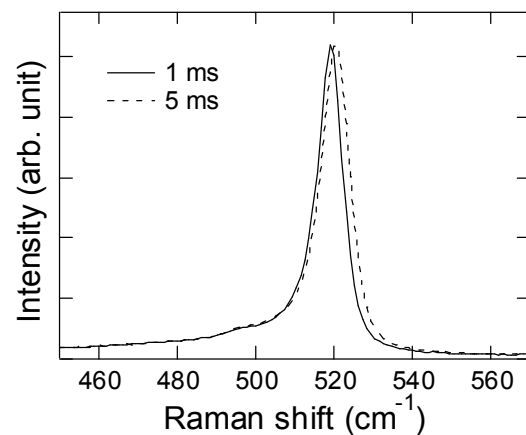

Figure 3 Raman spectra of poly-Si films formed by FLA with pulse durations of 1 and 5 ms.

Figure 3 shows the Raman spectra of Si films after FLA with pulse durations of 1 and 5 ms. Broad peaks centered at 480 cm^{-1}, corresponding to a-Si, are hardly seen, and sharp c-Si peaks located at 520 cm^{-1} are dominant in the both spectra, indicating high crystalline fraction close to unity. The full width at half maximum (FWHM) of the c-Si peaks is approximately 7 cm^{-1} in the both spectra. Hence, the pulse duration of flash lamp light is found not to affect significantly the quality of poly-Si films.

Figure 4 shows the surface AFM images of Si films before and after FLA with 1 and 5 ms pulse durations. Periodic surface roughness in a lateral crystallization direction is seen only on the lamp-annealed Si film surfaces, indicating that the surface roughness is formed spontaneously during crystallization by FLA. The intervals of the periodic structures are approximately 1 μm, and the root-mean-square roughness (R_{rms}) of the poly-Si surface is approximately 120 nm. We have confirmed that the intervals and R_{rms} are not significantly influenced by the pulse duration of flash lamp light. We have also demonstrated that this large surface roughness can act effectively to decrease optical reflection [12, 13].

Figure 5 shows the cross-sectional TEM image of a poly-Si film formed by FLA with 5 ms duration. There
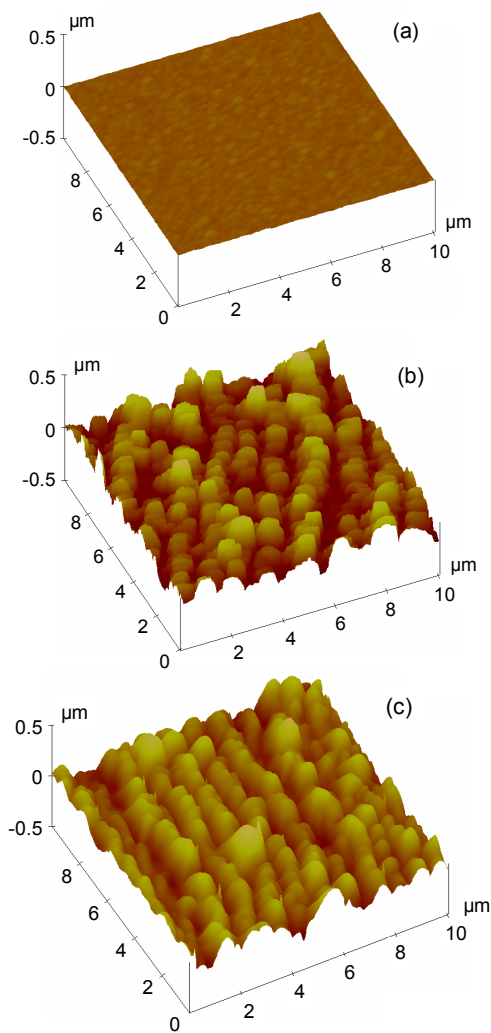
Figure 4 Surface AFM images of Si films. (a) before FLA, (b) after 1-ms-pulse FLA, (c) after 5-ms-pulse FLA.

Figure 5 Cross-sectional TEM image of a poly-Si formed by FLA with pulse duration of 5 ms.

exist periodic projections at approximately 1-µm intervals perpendicular to the lateral crystallization directions, also shown in the AFM image. The TEM image also indicates that the poly-Si films typically consist of two characteristic regions alternatively appearing in the lateral directions; large-grain regions containing relatively large grains more than 100 nm in size, and fine-grain regions consisting only of 10-nm size small grains. The former connects to the surface projections, whereas the latter links to the flat regions. In the large-grain regions, nonspherical grains stretched in the lateral crystallization direction are also seen. These complicated periodic microstructures inside a poly-Si film are also formed spontaneously through a crystallization process triggered by FLA.

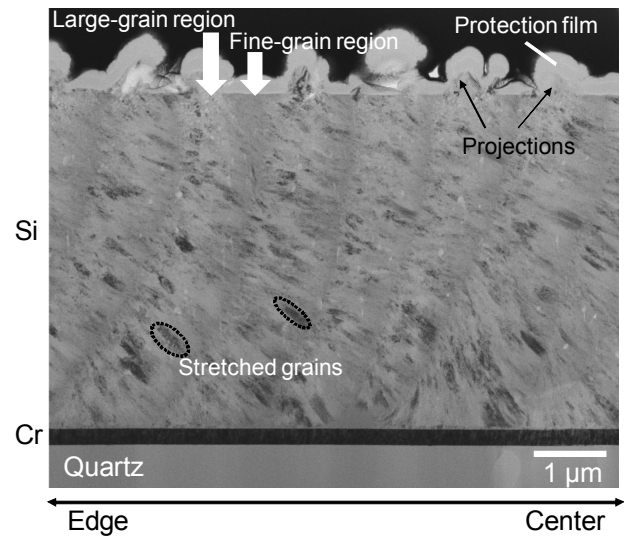**4 Discussion** The characteristic lateral crystallization observed in the FLA of a-Si films can be fully described as "Explosive Crystallization" (EC), whose mechanism is based on the propagation of heat, corresponding to an enthalpy difference between a-Si and c-Si phases, into neighboring uncrystallized a-Si regions [14]. The EC generally takes place with lateral crystallization velocities on the order of m/s [14], which completely corresponds to the value estimated above. The reason for the ignition of lateral crystallization at the sample edges is that the temperature of Si at the edges becomes higher than other parts because of receiving additional flash irradiation on the side surfaces. Once crystallization starts at the edges, the crystallized parts emit heat corresponding to the difference of enthalpy between a-Si and c-Si phases, which diffuse into neighboring a-Si, and induce further crystallization. The lateral crystallization therefore progresses by sequentially repeating the heat emission due to crystallization and its diffusion into neighboring a-Si.

The characteristic periodic structures may be caused by the two different crystallization modes. It is known that there are four types of the ECs; explosive liquid-phase epitaxy (ELPE), explosive liquid-phase nucleation (ELPN), explosive solid-phase epitaxy (ESPE), and explosive solid-phase nucleation (ESPN) [14]. Of these EC modes, ESPN is most likely in the system discussed here, judging from the existence of remarkably dense fine grains. However, the formation of surface projections and stretched grains cannot be explained by the simple ESPN, and the melting of the large-grain regions must be considered. During the lateral crystallization process, a-Si regions close to the heat-emitting poly-Si receive more heat than relatively distant a-Si regions, and can be heated up to its melting point of 1145 °C [15], resulting in the partial melting of a-Si. The neighboring a-Si may not completely melt because of its large latent heat of fusion of a-Si (35.4 kJ/mol) [15]. The stretched grains probably result from liquid-phase epitaxy to solid-phase-nucleated small grains. The surface
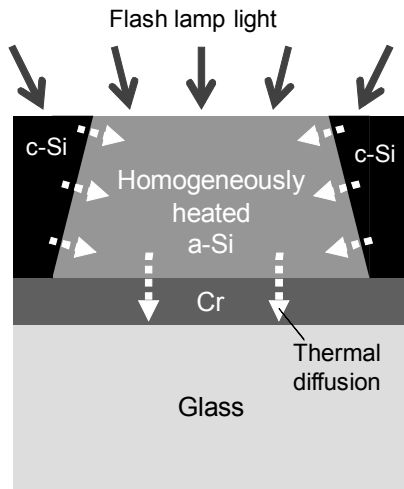
Figure 6 Schematic diagram of thermal flow during the lateral crystallization induced by FLA.

projections may be formed as a result of compressive stress applied to the Si film through the crystallization process due to the higher temperature of the Si film than a glass substrate, and/or the volume expansion of Si in the phase transition from liquid to solid. More detailed quantitative discussion concerning the crystallization mechanism is summarized elsewhere [16].

Based on the proposed crystallization mechanism, we can consistently describe the pulse duration dependence of lateral crystallization length. Figure 6 schematically shows the schematic diagram of thermal flow during the lateral crystallization induced by FLA. a-Si is homogeneously heated due to flash irradiation from the surface. On the other hand, there also exists thermal conduction, which cools a-Si down, from a-Si to a glass substrate through a Cr film. Hence, the lateral crystallization never continues permanently, and will stop when the temperature of a-Si in the vicinity of c-Si, which is decided by both homogeneous heating from flash irradiation and thermal diffusion from c-Si, falls below a threshold temperature needed for crystallization. Therefore, crystallization using longer pulse duration, which can keep the temperature of a-Si sufficiently high in longer time, results in longer lateral crystallization length.

5 Summary Flash-lamp-induced crystallization of precursor a-Si films a few μm thick progresses laterally at a remarkably high speed on the order of m/s, which is understood as the EC, that is, the propagation of heat into neighboring uncrystallized a-Si regions generated due to crystallization. This lateral crystallization leaves behind periodic structures at approximately 1-μm intervals perpendicular to the lateral crystallization directions on the surface of and inside the Si films. The existence of a number of small grains indicates that the crystallization is mainly governed by ESPN, whereas the formation of

stretched grains and surface projections derive from the partial melting of a-Si. The experimental result of the shorter lateral crystallization length in FLA with shorter pulse duration is consistent with the understanding of the crystallization mechanism based on the EC.

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