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Description	

Polycrystalline Silicon Films with Nanometer-Sized Dense Fine Grains Formed by Flash-Lamp-Induced Crystallization

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Abstract

Flash lamp annealing (FLA) with millisecond-order pulse duration can crystallize μm-order-thick a-Si films on glass substrates through explosive crystallization (EC), and flash-lamp-crystallized (FLC) poly-Si films consist of densely-packed nanometer-sized fine grains. We investigate the impact of the hydrogen concentration and the defect density of precursor a-Si films on crystallization mechanism and the microstructures of FLC poly-Si films, by comparing chemical-vapor-deposited (CVD) and sputtered precursor a-Si films. Transmission electron microscopy (TEM) observation reveals that FLC poly-Si films with similar periodic microstructures are formed by the FLA of the two kinds of precursor films, meaning no significant influence of hydrogen atoms and defect density on crystallization mechanism. This high flexibility of the properties of precursor a-Si films would contribute to a wide process window to reproducibly form FLC poly-Si films with the particular periodic microstructures.

Keyword: flash lamp annealing, crystallization, polycrystalline silicon, thin-film solar cell, nanometer-sized grains, sputtering

1. INTRODUCTION

Crystalline silicon (c-Si) thin films have been a promising material for next-generation solar cells, because of reduced Si material consumption and resulting cost reduction as well as the overcoming of light-induced degradation. Of a number of approaches to form thin c-Si, the crystallization of precursor amorphous Si (a-Si) films has realized a most advanced achievement of more than 10%-efficiency solar cells so far.[1] The process to form polycrystalline Si (poly-Si) films is, however, based on the solid-phase crystallization of precursor a-Si films through time-consuming conventional furnace annealing, which results in low fabrication throughput. Thus, we need to establish the method of rapidly crystallizing precursor a-Si films to form device-quality c-Si films. Another requirement for the rapid crystallization of a-Si films is to avoid thermal damage to substrates with poor thermal tolerance.

Flash lamp annealing (FLA) is a millisecond-order annealing technique using pulse light from a Xe lamp array.[2] Millisecond-order annealing results in thermal diffusion lengths of 10-100 μm both for a-Si and glass, which enables us to crystallize μm-order-thick a-Si films, required for the sufficient absorption of sunlight, and to prevent the heating of whole glass substrates with a thickness of typically ~1 mm. We have confirmed that poly-Si films with a thickness of more than 4 μm can be formed by FLA of catalytic chemical vapor deposited (Cat-CVD) a-Si films on quartz and soda lime glass substrates. Flash-lamp-crystallized (FLC) poly-Si films contain 10-nm-sized densely-packed fine grains as well as relatively large-sized (>100 nm) grains, which results from explosive crystallization (EC), lateral crystallization driven by the release of latent heat.[3] This densely-packed structure would contribute to the low concentration of oxygen ($<10^{19}$ /cm^3) that invades from atmosphere into grain boundaries. EC induced by FLA has been found to leave behind periodic microstructures along lateral crystallization directions with an interval of ~1 μm.[3] This periodic microstructure can act to effectively reduce optical reflection on the surface of FLC poly-Si films,[4] and we should know the impact of the properties of precursor a-Si films on crystallization mechanism and on resulting microstructures in order to reproducibly form FLC poly-Si films with similar microstructures.

In this study, we have attempted FLA of sputtered a-Si films, as well as Cat-CVD a-Si films, in order to know the effect of hydrogen and defect density on crystallization mechanism and the microstructure of FLC poly-Si films. We have confirmed that EC takes place also in sputtered a-Si films, and leaves behind periodic microstructures similar to the case of Cat-CVD a-Si precursor films, which means no significant impact of precursor films on crystallization mechanism.

2. EXPERIMENTAL DFTAILS

We first deposited 60-200 nm-thick Cr films by sputtering on some of quartz glass substrates with a size of 20 mm × 20 mm × 0.7 mm. These Cr films were just for improvement in the adhesion of Si films to glass. We then deposited 2-3 μm-thick a-Si films by two methods: Cat-CVD and RF sputtering. The detailed deposition conditions of Cat-CVD have been summarized elsewhere.[5] Electron spin resonance (ESR) measurement revealed that sputtered a-Si films had initial defect density of $\sim 5\times10^{19}$ /cm^3, which was much higher than that of Cat-CVD films of $\sim 1\times10^{16}$ /cm^3. Another critical difference in the two a-Si was hydrogen contents. Cat-CVD a-Si films contained hydrogen atoms on the order of 10^{21} /cm^3, whereas sputtered a-Si films had no intentionally-included hydrogen atoms and no remarkable peaks related to Si-H bonds were seen in Fourier transform infrared spectroscopy (FT-IR) spectra.

FLA was performed using a 5 ms-duration pulse light emitted from a Xe lamp array. Only one shot of flash irradiation was supplied for each sample under preheating with a ramp rate of approximately 400 ºC/min and following heating at constant temperature of 400 ºC for about 5 min. We performed no dehydrogenation process prior to FLA. The surfaces of FLC poly-Si films were characterized by using differential interference contrast microscopy. We used Raman spectroscopy with a 632.8 nm line of a He-Ne laser in order to confirm crystallization and to investigate crystalline fraction of FLA Si films. The detailed microstructures and the electron-beam diffraction (EBD) patterns of FLC poly-Si films were also observed with a JEOL JEM-4000EX transmission electron microscope (TEM) operating at 400 keV after thinning the cross section of an FLC poly-Si film by focused ion beam. The dangling bond density of FLC poly-Si films was also characterized with an ESR system using FLC poly-Si films formed directly on quartz glass substrates.

3. RESULTS AND DISCUSSION

Figure 1 shows the surface optical microscopic image of an FLC poly-Si film formed from a sputtered a-Si film. One can clearly see periodic surface microstructures with an interval of ~1 μm along a lateral crystallization direction. These particular microstructures are also seen on the surface of FLC poly-Si films formed from Cat-CVD a-Si precursor films, and can be considered to result from EC.[3] As has been reported, there are several kinds of EC categorized by the mechanism of nucleation and grain growth,[6-8] and we have also confirmed that the mode of EC can change in crystallization by FLA depending on the thickness of precursor a-Si films and FLA configurations.[9] In this experiment, sputtered a-Si films had a thickness same as those of Cat-CVD a-Si films, and FLA was performed under a same configuration, in which FLA results in the formation of poly-Si films with equivalent surface microstructures. This fact means that EC occurs in a same crystallization mechanism in both sputtered and Cat-CVD a-Si films.

Figure 2 shows the Raman spectra of FLA poly-Si films formed from sputtered and Cat-CVD a-Si films. The spectrum of an FLC poly-Si film formed from a sputtered a-Si film shows high crystalline fraction close to unity, and the full width at half maximum (FWHM) of a c-Si peak of ~7 cm^{-1} is slightly larger than but almost equivalent to that of an FLC poly-Si film formed from Cat-CVD a-Si films. This FWHM of the c-Si peak larger than that of c-Si wafers (~4 cm^{-1}) is due to the existence of a number of nanometer-sized grains in these films.[10] One can see slight (~1 cm^{-1}) shift of a c-Si peak for an FLC poly-Si film formed from a sputtered a-Si film to larger wavenumber, which means the existence of compressive stress in it.[11] This might be because sputtered a-Si films originally have compressive stress.

Figure 3 shows the cross-sectional TEM image of an FLC poly-Si film formed from a sputtered a-Si film. The periodic microstructures are seen also inside the poly-Si, and connect to the surface structures. One can see two typical regions: one connects to surface projections and contains 100-nm-sized large grains stretched to a lateral crystallization direction, and the other links to flat surface parts and contain no

100-nm-sized grains. These typical microstructures can also be seen in FLC poly-Si films formed from Cat-CVD a-Si films.[3] We have previously discussed that the former region, large-grain region, is formed through solid-phase nucleation (SPN) and partial liquid-phase epitaxy, whereas the latter region, fine-grain region, is formed through SPN without liquid-phase process.[3] Figure 4 shows the EBD patterns of the large-grain and the fine-grain regions of an FLC poly-Si film formed from a sputtered a-Si film. The EBD pattern of the large-grain region contains a number of bright spots, whereas clear multi-ring patterns are seen in the EBD pattern of the fine-grain region. This indicates that the large-grain regions contain larger and more oriented grains than the fine-grain regions. Figure 5 shows the bright-field and the dark-field TEM images of the large-grain region of an FLC poly-Si film formed from a sputtered a-Si film. One can actually confirm the existence of ~100-nm-sized grains in the large-grain region. On the contrary, in the bright-field and the dark-field TEM images of the fine-grain region, shown in Fig. 6, no 100-nm-sized large grains are observed. These TEM observation results are also equivalent to those of FLC poly-Si films formed from Cat-CVD a-Si films.[12] We can therefore conclude that the impact of the hydrogen atom concentration and the defect density of precursor a-Si films on crystallization mechanism is not significant. This high flexibility of the properties of precursor a-Si films would lead to high reproducibility of forming FLC poly-Si films with the particular periodic microstructures available to reduce optical reflection.

Finally, we will discuss the applicability of FLC poly-Si films formed from sputtered and CVD precursor a-Si films to solar cells. Figure 7 shows the surface images of FLC poly-Si films formed from sputtered and Cat-CVD a-Si films directly prepared on quartz glass substrates. The use of a Cat-CVD a-Si film results in the partial peeling of Si during FLA, as has been reported previously.[13] On the contrary, sputtered a-Si can be crystallized by FLA without serious peeling of Si even with no assistance of a Cr adhesion layer. This high adhesion is probably due to the absence of hydrogen atoms in a precursor film. We have confirmed that Cat-CVD a-Si films formed directly on quartz glass substrates can also be crystallized without Si film peeling after dehydrogenation, and thus, hydrogen atoms may affect the peeling of Si films during FLA.[12] Since Cr atoms act as recombination centers for minority carriers in c-Si,[14] it is favorable to fabricate solar cells without Cr films, which could be realized by using a-Si films with sufficiently low hydrogen contents. On the other hand, we have found that poly-Si films formed from sputtered a-Si films has much larger number of defects with a density of more than 10^{18} /cm^3 than those formed from Cat-CVD a-Si films whose defect density can be down to 5×10^{16} /cm^3.[15] Since their microstructures are similar, as shown above, the difference of defect density is probably due to the effect of defect termination by hydrogen atoms. The remarkably rapid lateral crystallization driven by EC leads to the suppression of desorbing hydrogen atoms during crystallization, and remaining hydrogen atoms may terminate Si dangling bonds.[16] We have also confirmed that the post furnace annealing of FLC poly-Si formed from Cat-CVD a-Si films results in significant decrease in defect density, which is probably due to the enhancement of defect termination effects by remaining hydrogen atoms.[15] This effect is a unique advantage of FLC poly-Si films formed from CVD films, and should be utilized to realize high-quality poly-Si films. It may therefore be favorable to prepare a-Si films with a hydrogen concentration controlled to a level so that Si film peeling is suppressed and defect density can be sufficiently low.

4. SUMMARY

We have clarified that sputtered a-Si films, with much more defects and much less hydrogen than Cat-CVD a-Si films, can also crystallize by FLA through EC, and poly-Si films formed from sputtered a-Si films have periodic microstructures and grain features similar to those formed from Cat-CVD a-Si films. This indicates that the impact of hydrogen atoms and defects on crystallization mechanism is not significant. The high flexibility of the properties of precursor a-Si films would result in the highly reproducible formation of FLC poly-Si films with periodic microstructures which can effectively act to reduce optical reflection.

Acknowledgements

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Figure Caption

Figure 1. Optical microscopic image of the surface of an FLC poly-Si film formed from a sputtered a-Si film. An arrow on the image indicates a lateral crystallization direction.

Figure 2. Raman spectra of FLA poly-Si films formed from sputtered and Cat-CVD a-Si films.

Figure 3. Cross-sectional TEM image of an FLC poly-Si film formed from a sputtered a-Si film. Solid and dashed arrows indicate fine-grain and large-grain regions, respectively.

Figure 4. EBD patterns of (a) the large-grain and (b) the fine-grain regions of an FLC poly-Si film formed from a sputtered a-Si film.

Figure 5. (a) Bright-field and (b) dark-field TEM images of the large-grain region of an FLC poly-Si film formed from a sputtered a-Si film.

Figure 6. (a) Bright-field and (b) dark-field TEM images of the fine-grain region of an FLC poly-Si film formed from a sputtered a-Si film.

Figure 7. Surface images of FLC poly-Si films formed from (a) a sputtered a-Si film and (b) a Cat-CVD a-Si film.

Figure 1.

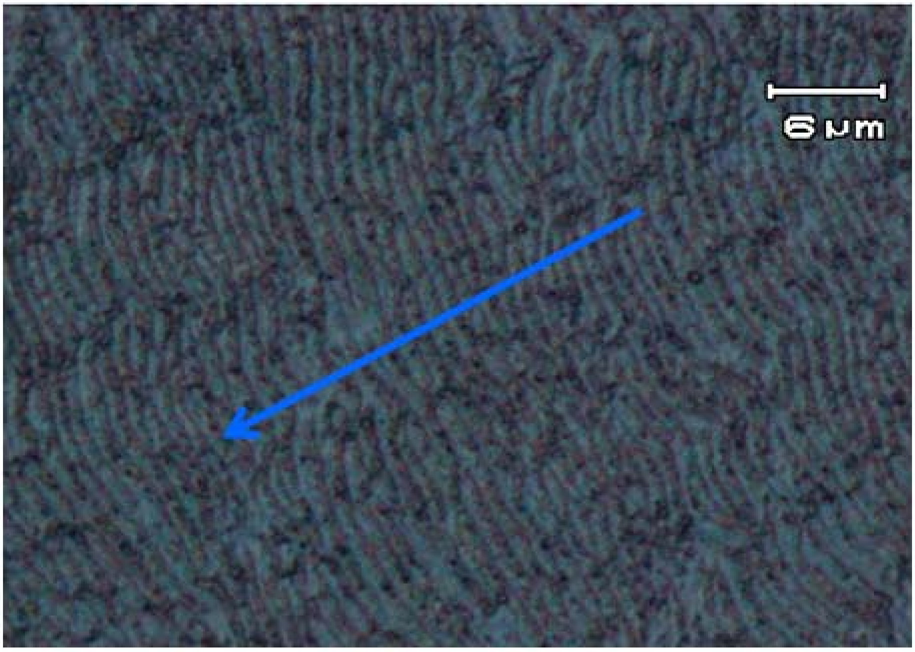

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Figure 2.

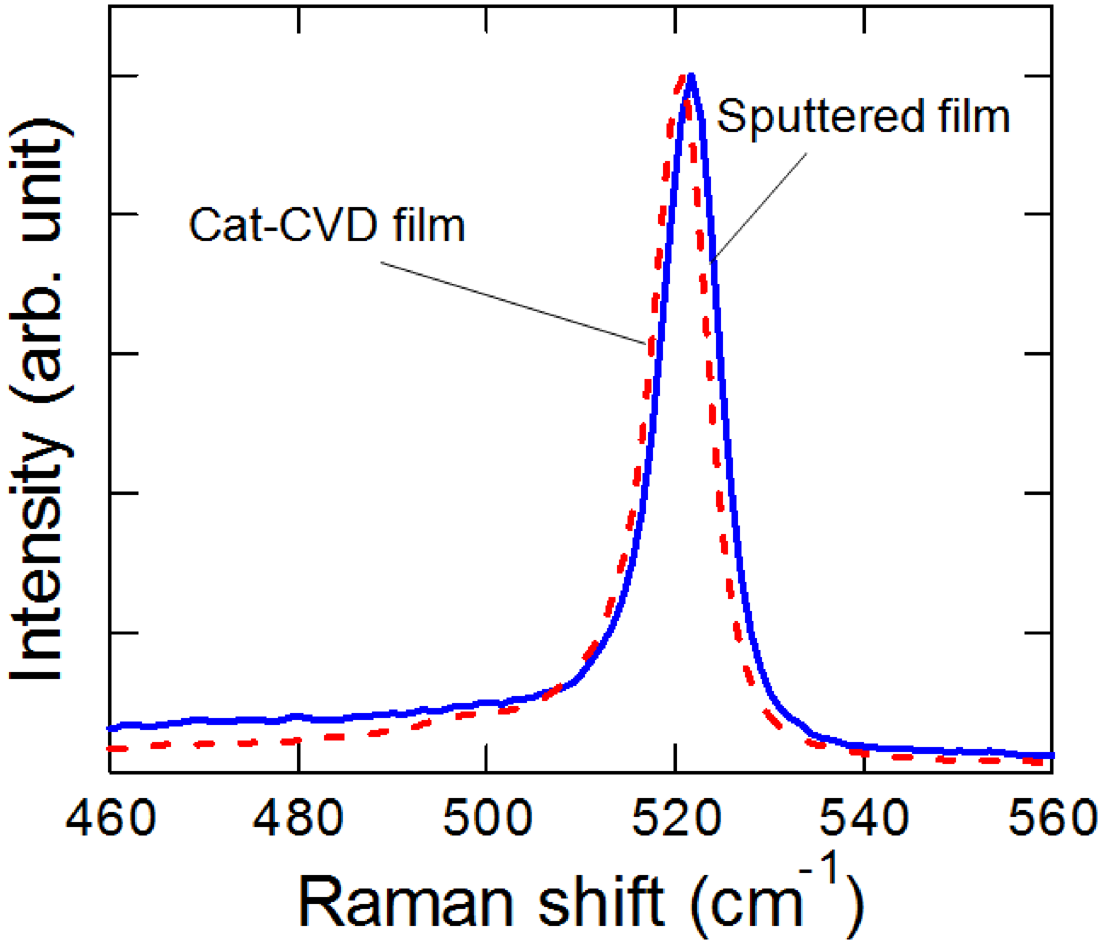

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Figure 3.

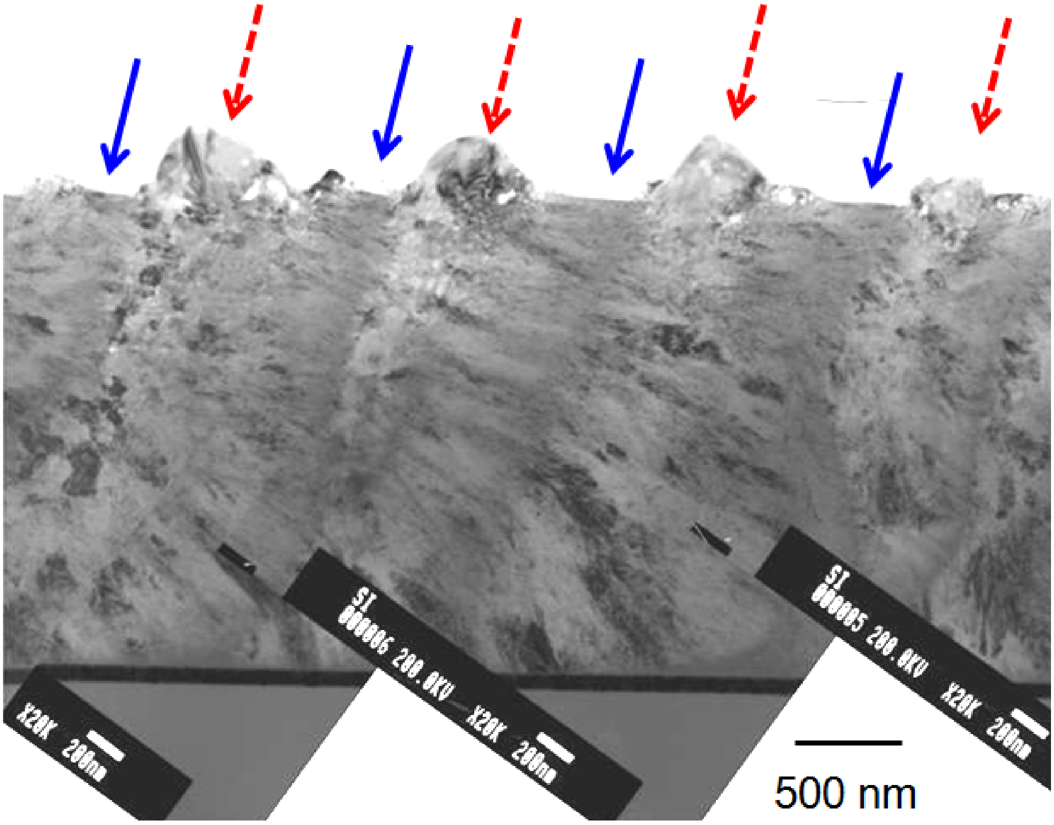

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Figure 4.

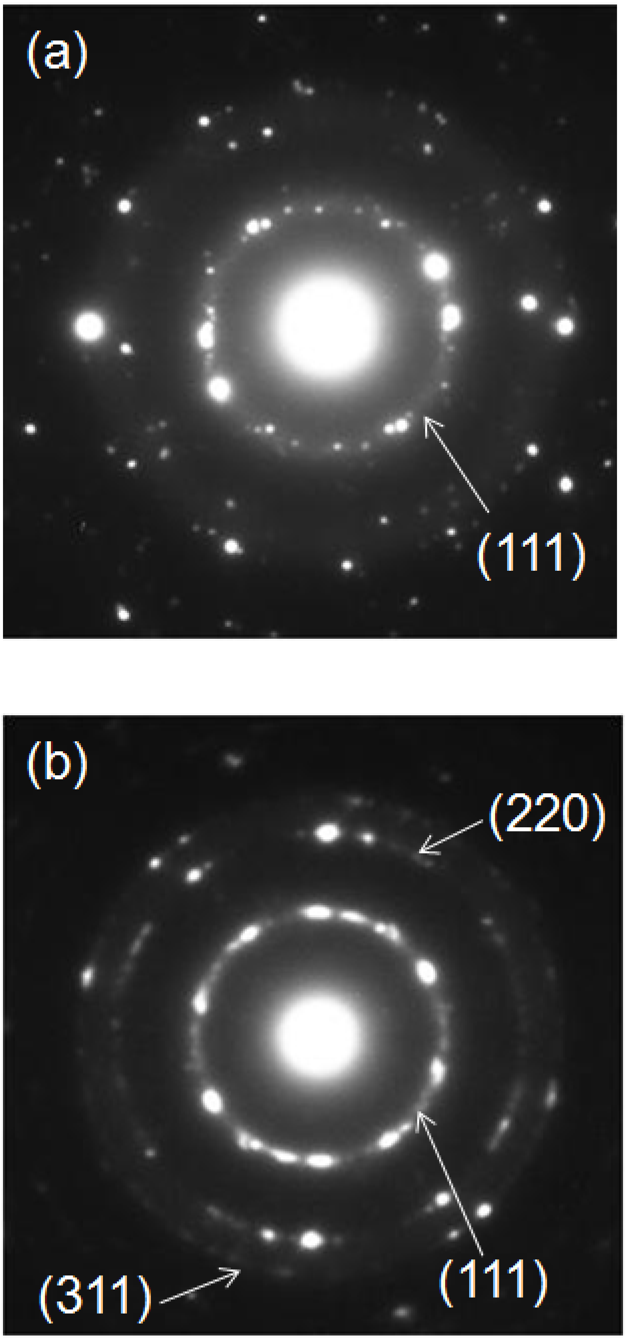

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Figure 5.

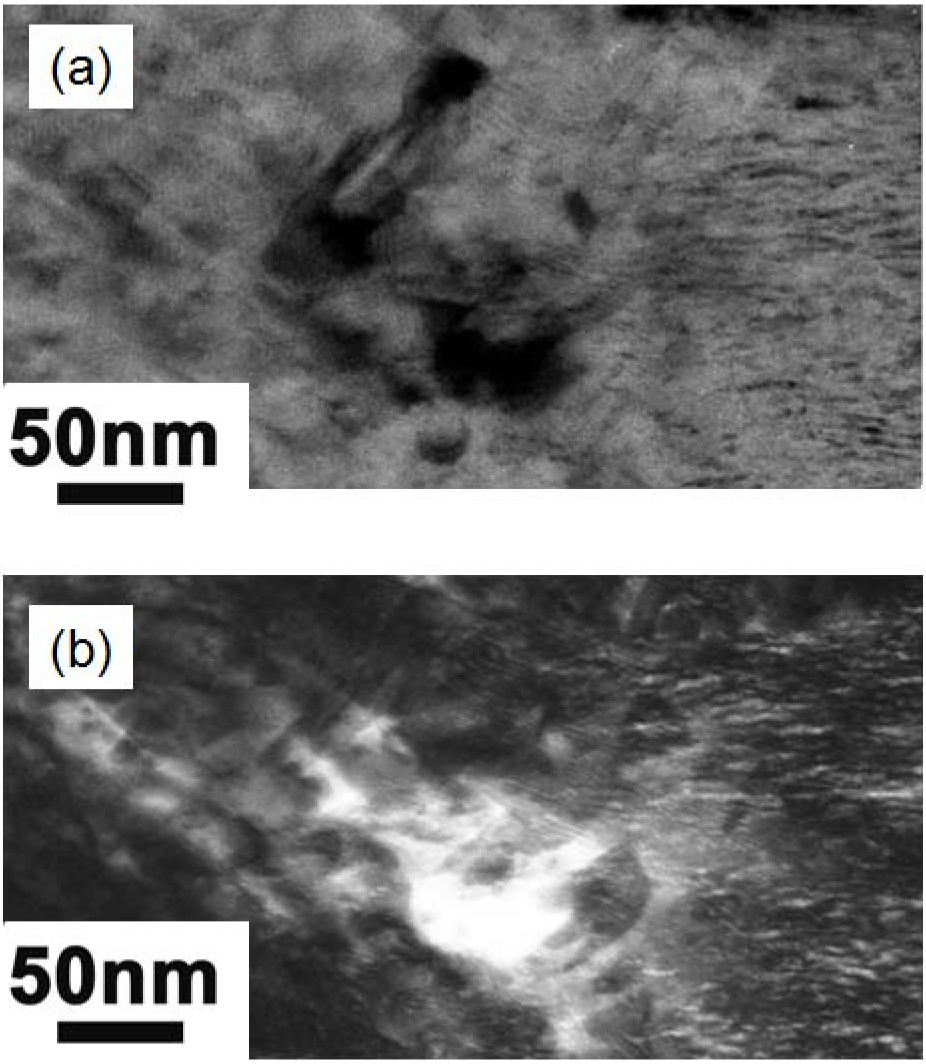

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Figure 6.

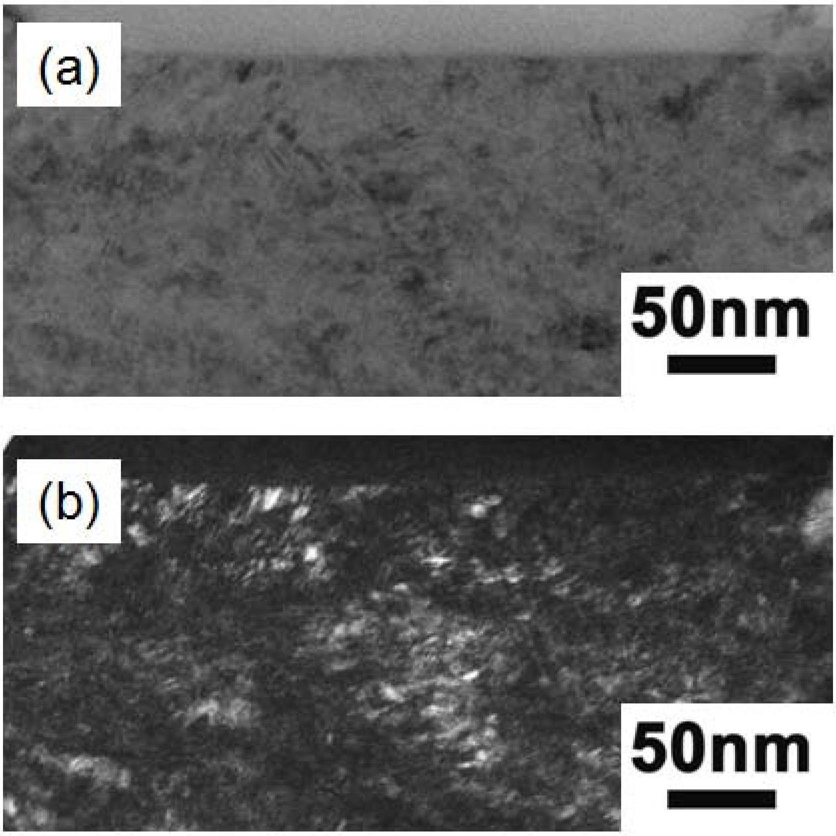

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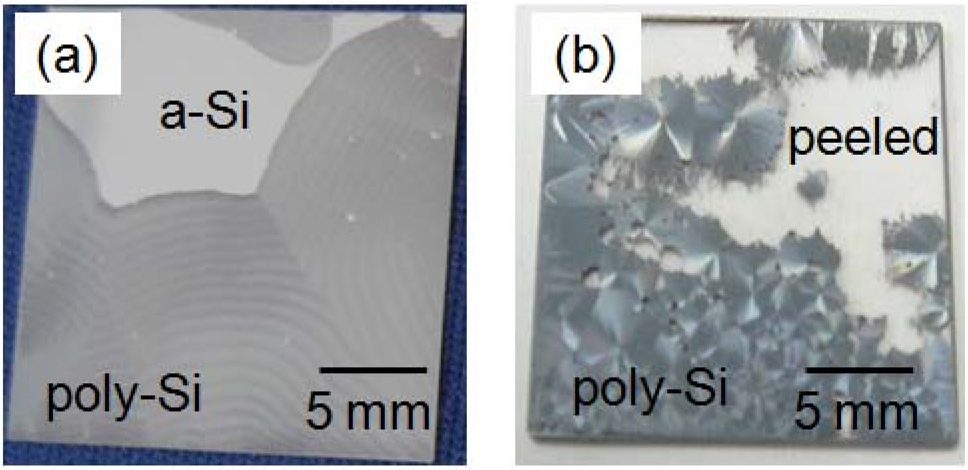
Figure 7.



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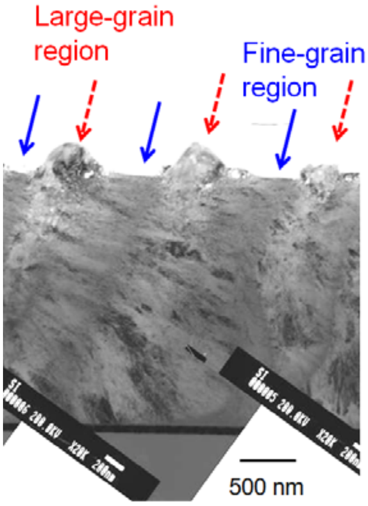

The use of sputtered amorphous silicon (a-Si) films for precursor films of flash-lamp-induced crystallization leads to the formation of polycrystalline Si (poly-Si) films with periodic microstructures, as is the case in catalytic chemical-vapor-deposited (Cat-CVD) hydrogenated a-Si films. This fact indicates no significant influence of hydrogen atoms and defect density on the particular crystallization mechanism.