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Description	

Formation of Highly Uniform Micrometer-Order-Thick Polycrystalline Silicon Films by Flash Lamp Annealing of Amorphous Silicon on Glass Substrates

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Polycrystalline silicon (poly-Si) films as thick as 4.5 μm are prepared by flash lamp annealing (FLA) of amorphous silicon (a-Si) films without thermal damage onto glass substrates. The a-Si films are deposited by catalytic chemical vapor deposition (Cat-CVD) at 320 $^{\circ}\text{C}$. Since the hydrogen content in Cat-CVD a-Si films is as low as 3 at. %, they are easily converted to poly-Si without any dehydrogenation treatment. Chromium (Cr) films 60 nm thick are coated onto glass substrates to achieve high area uniformity of poly-Si formation. Secondary ion mass spectroscopy (SIMS) reveals that no diffused Cr atoms are detected inside poly-Si films and that crystallization is not the well-known metal-induced crystallization. Raman spectra from the poly-Si films show high crystallinity close to 1, and the photoluminescence (PL) spectrum demonstrates

clear band-to-band transition, indicating the formation of device-quality poly-Si by FLA of Cat-CVD a-Si.

KEYWORDS: flash lamp annealing, millisecond treatment, crystallization, poly-Si, solar cell

1. Introduction

Photovoltaic systems have been expected to be a candidate for the generation technology of renewable energy. Although crystalline silicon (c-Si) solar cells currently hold a market share of more than 90%, fabrication costs are still high and thus, further development of cost-effective fabrication processes of high-efficiency solar cells is desired. Thin-film solar cells consisting of amorphous-Si (a-Si), microcrystalline Si ($\mu\text{c-Si}$), and their stacked structure formed by plasma-enhanced chemical vapor deposition (PECVD) can be directly fabricated on low-cost glass substrates with a smaller amount of materials and thus with lower fabrication cost. However, they show relatively low conversion efficiency due to a shorter minority carrier diffusion length than that of c-Si because of the a-Si phases included even in $\mu\text{c-Si}$. To form thin-film polycrystalline Si (poly-Si) with high crystallinity, post-crystallization of micrometer-order-thick a-Si films, such as by furnace annealing for several hours or more¹⁻³⁾ and rapid thermal annealing (RTA) for several ten seconds^{4,5)} have been investigated. However, to improve productivity and to avoid thermal damage to the low-cost glass substrates, such crystallization should be performed within several milliseconds. This is because the thermal diffusion length of a-Si exceeds 10 μm in such a time period, whereas those of glass are suppressed to less than 100 μm . Thus

micrometer-order-thick a-Si is expected to be crystallized without the heating of the whole glass substrate. Flash lamp annealing (FLA)⁶⁻⁸⁾ and plasma jet crystallization (PJC)⁹⁻¹¹⁾ can realize such millisecond treatment. We have reported experimental studies of the crystallization of 1.5- μm -thick a-Si deposited by catalytic chemical vapor deposition (Cat-CVD) directly onto quartz substrates by means of FLA followed by defect termination by high-pressure water-vapor annealing (HPWVA).^{12, 13)} Although the poly-Si films show long carrier lifetimes of more than 5 μs , the area homogeneity of crystallinity is imperfect. Thicker poly-Si films, which are required for effective optical absorption, have not been formed because of peeling of the Si films during FLA. Furthermore, considering the practicality of thin-film solar cells fabricated using this poly-Si film, the formation of a back electrode as well as a back reflector is necessary.

In this paper, we report on the crystallization of a-Si with thicknesses of 3-4.5 μm deposited on metal-coated glass substrates. The quality of the poly-Si films is also characterized in detail.

2. Experimental Procedure

The sample structure is schematically illustrated in Fig. 1. Chromium (Cr) films of 60 nm in thickness were first deposited on $20 \times 20 \times 0.7 \text{ mm}^3$ glass substrates by

sputtering at room temperature. Both quartz and sodalime glasses were used as substrates. Although the polycrystallization of a-Si films has been confirmed on both types of substrates, we concentrate on demonstrating the results using quartz glass substrates in this paper in order to understand the fundamental phenomena of crystallization by FLA. Precursor a-Si films were deposited on the Cr-coated surface by Cat-CVD at 320 °C. The hydrogen content in the deposited films was as low as 3%, so that hydrogen bubbling during FLA, and thus issues of ablation or peeling of Si films, can be significantly alleviated. Therefore, no dehydrogenation treatment was performed before FLA. The a-Si thickness was fixed at 3.0 and 4.5 μm .

The pulse width of flash lamp irradiation was fixed at less than 10 ms, whereas lamp irradiance, whose exact energy was, unfortunately, unknown due to a lack of a measurement method, was systematically changed to find the optimum value for crystallization. Only one pulse irradiation was supplied to each sample. Crystallization of the films and their crystallinity were characterized by Raman spectroscopy with a He-Ne laser of 632.8 nm in wavelength, which corresponds to the penetration length of about 3 μm for c-Si. Before the measurement of lamp-annealed samples, a reference monocrystalline Si wafer was measured and its peak was set to be 520 cm^{-1} . Photoluminescence (PL) measurement was performed at 4.4 K using a

solid-state laser of 532 nm in wavelength. The diffusion of Cr was checked by secondary ion mass spectroscopy (SIMS).

3. Results and Discussion

Figure 2(a) shows the surface of lamp-annealed 3- μ m-thick Si films on the Cr-coated 20×20 mm² quartz substrates. The polycrystallization of a-Si without ablation can be seen as the silver-colored surface, which is in contrast to the case without Cr film, where partial ablation of Si has occurred, as shown in Fig. 2(b). One explanation for these phenomena is the improvement of lateral temperature homogeneity during FLA caused by the large thermal diffusivity of Cr compared with quartz. The thermal diffusion length L_T of Cr is estimated to be 0.34 mm from the equation $L_T = \sqrt{Kt / c\rho}$ using parameters at 1000 °C with thermal conductivity¹⁴⁾ $K = 0.60$ W/(cm·K), specific heat¹⁵⁾ $c = 0.71$ J/(g·K), density¹⁵⁾ $\rho = 7.19$ g/cm³ and diffusion time $t = 10$ ms. On the basis of this estimation, although the complete homogenization of temperature in a 20×20 mm² area seems to be difficult, the Cr film may reduce the extreme heat concentration at the edge of the Si film that otherwise causes the peeling or ablation of Si films. Another possibility is the improvement of the interface property upon changing the thermal expansion coefficient. Linear thermal expansion

coefficients of c-Si¹⁵⁾ and quartz¹⁶⁾ are about 5.1×10^{-6} and $4.1 \times 10^{-7}/\text{K}$ at 1000 °C, respectively, and thus poly-Si films on quartz substrates receive compressive stress during FLA. By inserting Cr with an expansion coefficient¹⁵⁾ of $1.2 \times 10^{-5} /\text{K}$ at 1000 °C, the total stress to the Si film tends to be compensated so that the ablation and peeling of Si films are suppressed. Adherence itself between films and substrates is also an important factor and this also might be improved by inserting the Cr film. Figure 2(c) shows the surface of the sample without Cr insertion subjected to the same lamp irradiance as that of the Cr-inserted sample. No noteworthy feature can be observed. The Raman spectrum from the film shows no c-Si phase. These are indications of an enhanced reflection of flash lamp irradiation by Cr films and a resulting increase in the optical absorption of flash lamp light in Si film.

Figure 3 indicates the Raman spectrum obtained from the sample with Si thickness of 3.0 μm that was shown in Fig. 2(a). A sharp peak at 520.4 cm^{-1} , which is almost the same Raman shift as the 520 cm^{-1} of the reference monocrystalline Si, dominates the spectrum and little evidence of the a-Si phase can be seen, indicating high crystallinity and crystal quality. We measured Raman spectra at other points in the same sample and outstanding area uniformity of crystallinity was confirmed, which was not observed when Cr film was not inserted. Figure 4 shows the PL spectrum of the 3.0- μm -thick

poly-Si film excited at a power density of about 1 W/cm^2 . Clear band-to-band transition related to free-exciton recombination assisted by transverse optical (TO) phonons is shown. This is also an indication of the high quality of the poly-Si.

Figure 5(a) shows the surface of $4.5\text{-}\mu\text{m}$ -thick Si on Cr-coated $20 \times 20 \text{ mm}^2$ quartz substrates treated under the optimum lamp irradiance. Polycrystallization without serious ablation is confirmed also for $4.5 \mu\text{m}$ -thick a-Si. Under lower lamp irradiance, partial crystallization occurs, as shown in Fig. 5(b). Interestingly, polycrystallization occurs in the lateral direction from the edges or randomly generated pits. Figure 5(c) shows a typical image of a pit having a diameter of about $20 \mu\text{m}$ as the starting point of the lateral crystal growth. Such pits do not exist before FLA and thus they must be generated during annealing. Surface images of the poly-Si films show grain-like features. On the other hand, Raman spectrum indicates a large full width at half maximum (FWHM) of 9.1 cm^{-1} . Therefore, we cannot conclude whether melting growth or solid-phase crystallization occurs. The generation mechanism of the pits is also unclear at the present time. However, we hypothesize the crystallization process to be as follows. At around the edges and the pits, the side of a-Si as well as the surface is irradiated during FLA. Thus a-Si around the edges and pits receives additional heating, so that nucleation or melting tends to occur there. Once nucleation

or solidification after melting occur, the extra generated heat due to the phase transition from the metastable a-Si state to the stable c-Si state diffuses to neighboring parts of a-Si, which causes further nucleation or melting. With higher lamp irradiation, the a-Si temperature rises and the lateral crystallization length during FLA becomes longer, resulting in complete crystallization of a-Si in the $20 \times 20 \text{ mm}^2$ area. The pits seem to be unsuitable for solar cell application. This issue can be resolved by making crystallization start only from the edges of the sample, which is possible by carefully tuning the lamp irradiance.

Figure 6 shows SIMS profiles of Cr atoms in the structure with 3.0- μm -thick Si film before and after FLA. No significant diffusion of Cr atoms into Si films is observed, and thus this coating metal probably does not degrade the Si films. Furthermore, these results imply that the crystallization is not the metal-induced crystallization (MIC). Additionally, even when a 300-nm-thick silicon nitride film is inserted between a-Si film and the Cr layer, crystallization still occurs in the same mode. This is additional evidence that FLA crystallization on the Cr layer is not MIC.

4. Conclusions

We have accomplished the crystallization of a-Si with thicknesses of 3.0 and 4.5 μm deposited on Cr-coated glass substrates by FLA. The inserted Cr films both suppress the ablation of Si and reflect lamp irradiation. The poly-Si shows high crystallinity close to 1 with excellent homogeneity in a $20 \times 20 \text{ mm}^2$ area. The crystallization occurs in the lateral direction, which may be explained by local heating and the resulting crystallization of a-Si around the edges or generated pits, followed by the transfer of excess heat to neighboring a-Si, which causes further crystallization. The inserted metal shows no serious diffusion into Si films, and it can be utilized as the back electrode as well as the back reflector in thin-film solar cell devices. This is another advantage of this structure for solar cell applications.

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Figure captions

Fig. 1 Schematic of the sample structure containing precursor a-Si and Cr film.

Fig. 2 Surface of lamp-annealed 3- μm -thick Si films (a) with and (b) without Cr insertion, treated under the same irradiation conditions, and (c) without Cr film treated under high lamp irradiance on $20 \times 20 \text{ mm}^2$ quartz substrates. The crystallized areas are seen as silver color, whereas black area indicates a-Si phase.

Fig. 3 Raman spectrum of 3- μm -thick Si film with Cr insertion. No significant variation of spectrum properties is seen in $20 \times 20 \text{ mm}^2$ crystallized area.

Fig. 4 PL spectrum of 3- μm -thick Si measured at 4.4 K. A clear luminescence peak related to band-to-band transition is observed. The broad peak located at 1.8 eV may be due to electron-hole drops.

Fig. 5 Surface of 4.5- μm -thick Si films on Cr-coated $20 \times 20 \text{ mm}^2$ quartz substrates after FLA under optimum (a) and low (b) lamp irradiance. (c) Optical microscopic image of a pinhole spontaneously generated during FLA.

Fig. 6 SIMS profiles of Cr atoms in 3- μm -thick Si structure before and after FLA. No serious diffusion of Cr atoms is seen even after FLA.

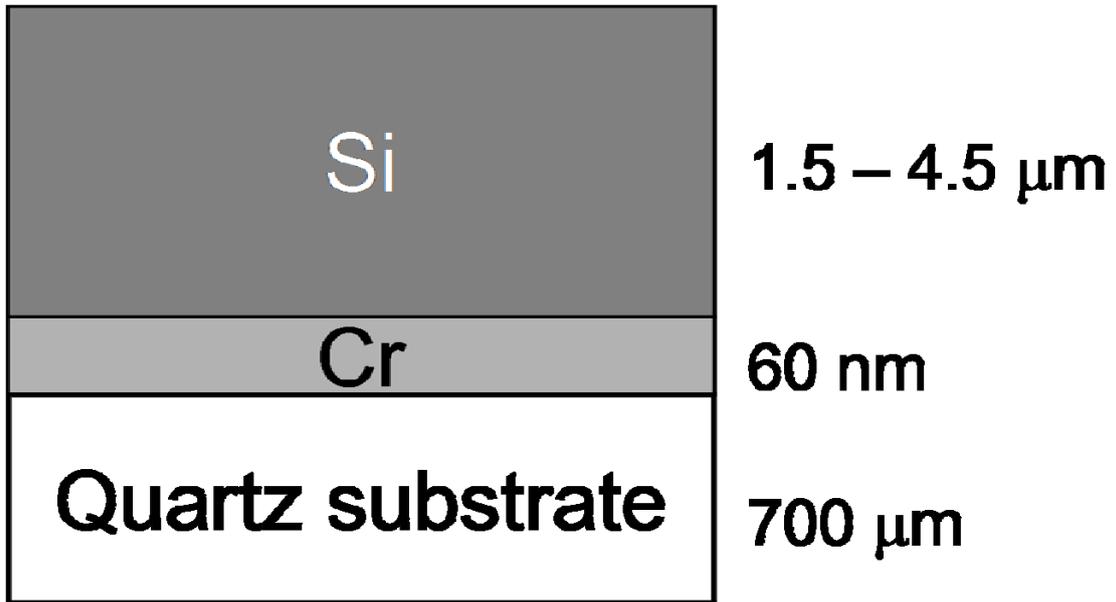


Figure 1 K. Ohdaira *et al.*,

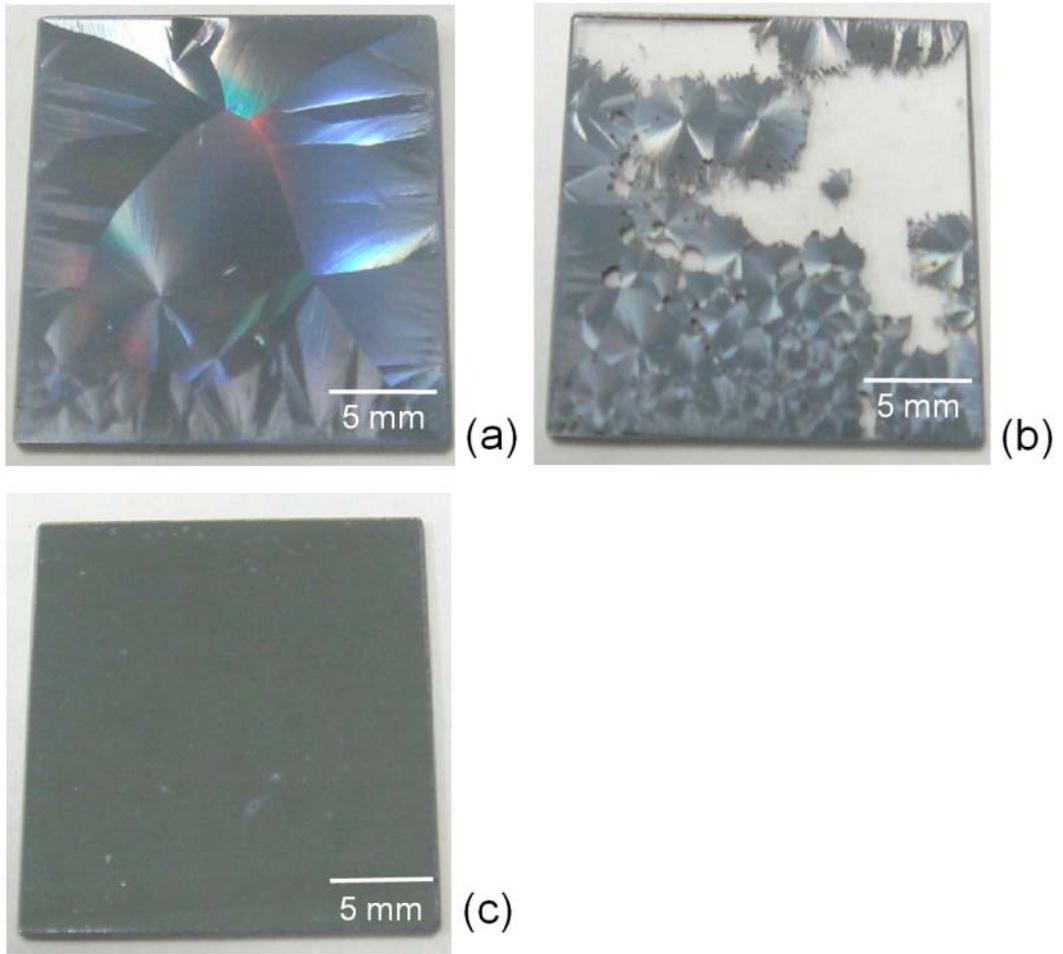


Figure 2 K. Ohdaira *et al.*,

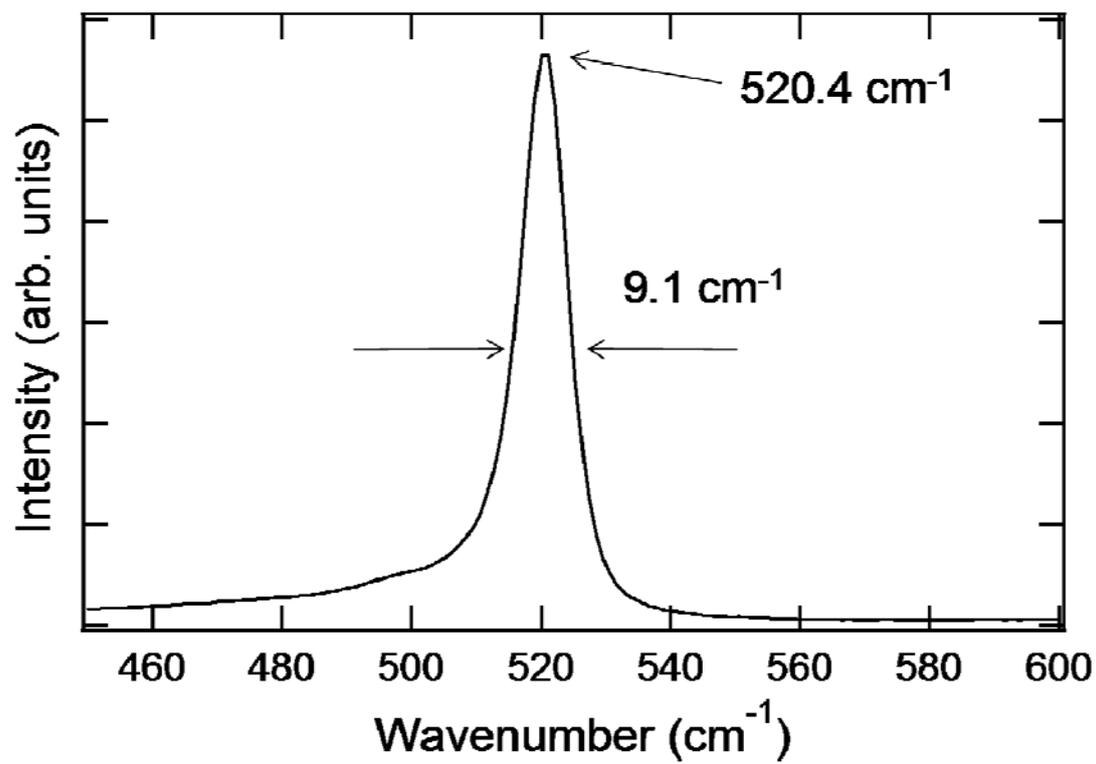


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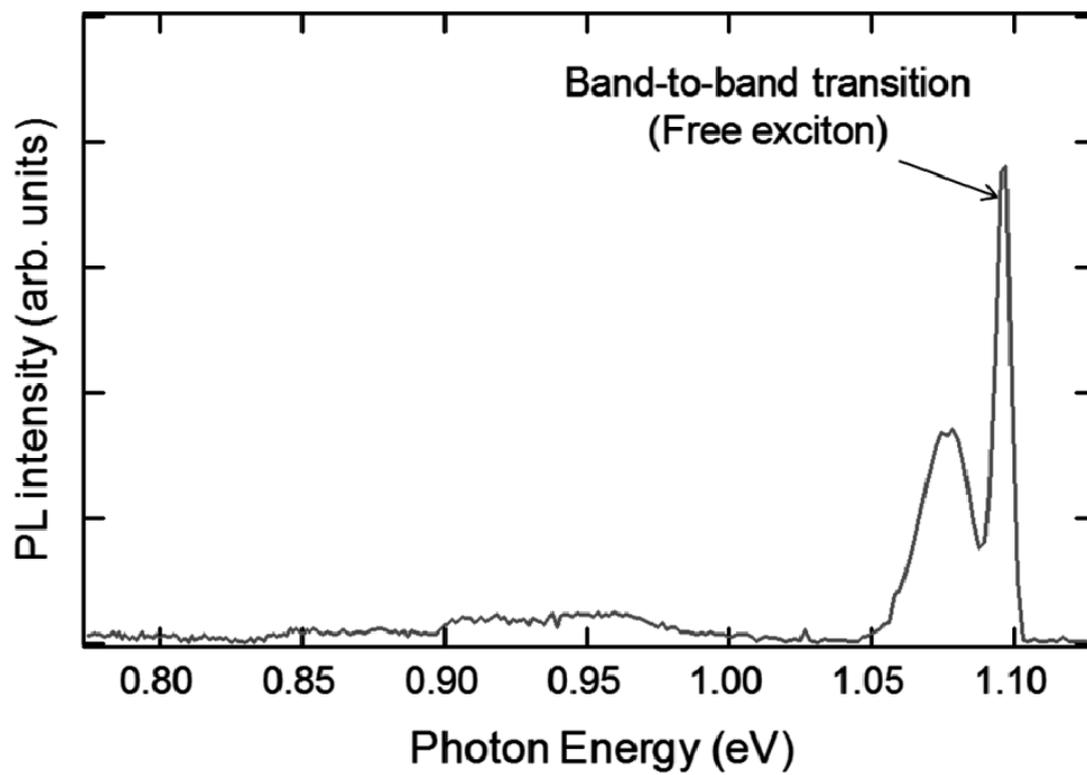


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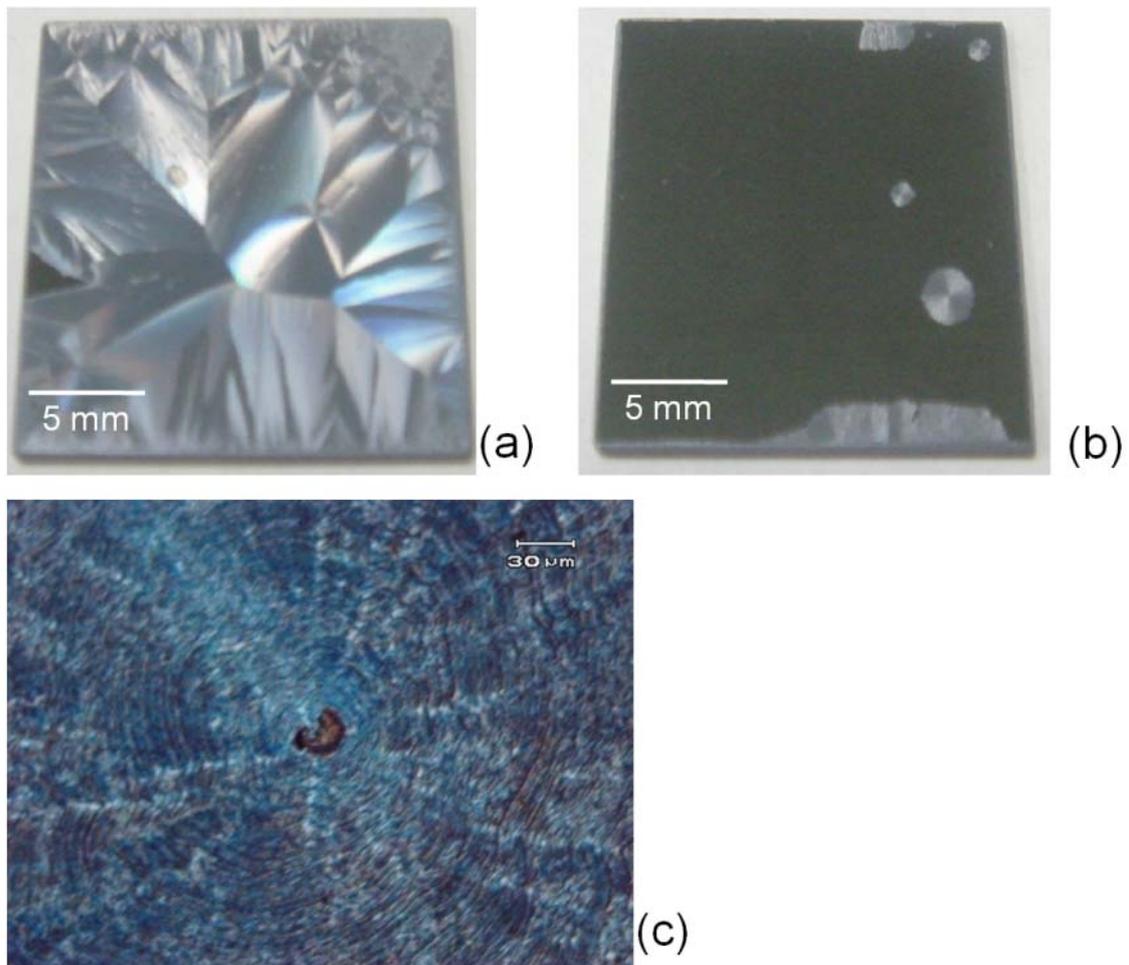


Figure 5 K. Ohdaira *et al.*,

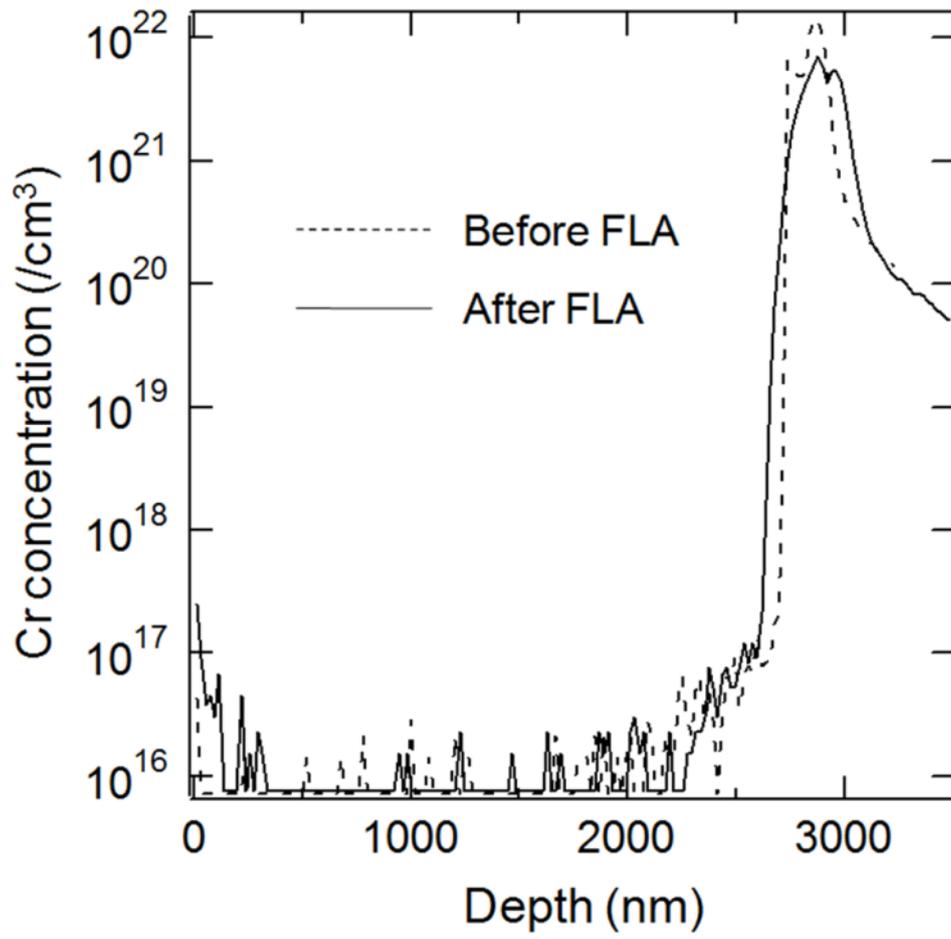


Figure 6 K. Ohdaira *et al.*,