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RAPID PUBLICATION

Influence of Laser Plasma Soft X-Ray Irradiation on Crystallization of a-Si Film by Infrared Furnace Annealing

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The influence of laser plasma soft X-ray (LPX) irradiation on crystallization of a-Si film by infrared (IR) furnace annealing is investigated. The crystallization temperature by LPX irradiation followed by IR annealing is lowered down to 420°C and the grain size increases up to 270 nm. This phenomenon is related with the change in characteristics of a-Si film which is generated by the bond distortion and relaxation during the LPX irradiation. It was found that the LPX-irradiated film is constituted by the two different layers and the refractive index of upper layer was lower than that of under layer. The dangling bond density of a-Si film was also decreased by LPX irradiation to a-Si film. From these results, the crystallization mechanism is discussed. [doi:10.2320/matertrans.M2010154]

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1. Introduction

It is important to crystallize amorphous silicon (a-Si) at low temperature for realization of flexible display, because the poly-Si is utilized as an active layer of thin-film transistor (TFT). So far, the process that the crystallized Si film on the glass substrate is transferred to the flexible substrate has been developed.[1)] It is a state-of-the-art process from a viewpoint of the realization of flexible display. However, it is not a practical method because of an increase of process step related to the Si film transfer and the additional cost corresponding to the process. The direct crystallization method other than the transfer method has also been examined as follows. The crystallization of a-Si film on the flexible substrate such as plastic, cellulose substrates by the excimer laser annealing (ELA) or green laser annealing has been challenged. It is thought that the laser crystallization damages the flexible substrate. Hard x-ray irradiation with a wiggler has been examined for the solid-phase epitaxy to grow dislocation-free silicon films.[2)] The temperature during crystallization rises up to approximately 500°C and the method is not suitable to the flexible substrates. We reported the low-temperature crystallization method by soft-x-ray irradiation using the synchrotron orbital radiation (SOR) facility, NewSUBARU.[3)] Because of the difference of brightness and absorption length between the soft and hard x-rays, the crystallization by soft x-ray was expected to proceed at low temperature. However, the obvious evidence of the crystallization was not identified because of the weak intensity of the x-ray beam. We presented the low-temperature crystallization of a-Si film utilizing a laser plasma soft X-ray (LPX) source[4)] followed by ELA.[5,6)] The photon density of the LPX is about ten times larger than that of the SOR light. The effect of LPX irradiation on crystallization of a-Si film by ELA was examined. It was found that LPX irradiation onto a-Si film before ELA decreases the threshold energy density of crystallization. It was also observed that Si atoms move on a-Si film surface by soft X-ray excitation using undulator source.[7)] It is inferred that the quasi-nuclei were formed in a-Si film during LPX irradiation. In this study, the characteristic of crystallized Si film by LPX irradiation followed by Infrared (IR) furnace annealing is examined. The structural change of a-Si film by LPX irradiation is examined by spectroscopic ellipsometry and electron spin resonance (ESR). From these results, the crystallization mechanism is discussed.

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2. Experimental Details

Amorphous Si film was deposited on SiO_2/glass substrates by plasma enhanced chemical vapor deposition (PECVD) method. The thickness of a-Si film was 50 nm. LPX was irradiated to a-Si film for 300 s (96000 shots) and 600 s (192000 shots) in vacuum at about 1×10^{-2} Pa. The distance from the light source to sample was 10 cm. LPX was emitted by Nd:YAG laser irradiation to solid Xe target, which was generated on the rotating copper-drum cooled by liquid nitrogen at −196°C. Repetition rate of LPX was 320 Hz. The wave length and photon energy of LPX was 10.8 nm and 115 eV. Substrate temperature was 115°C measured by thermo-tape pasted on the backside of substrate. A-Si films with and without LPX irradiation were annealed by IR furnace at 0.4 Pa for 1800 s. The structural property of crystallized Si film was measured by Raman scattering spectroscopy. Raman spectroscopy was carried out at room temperature using the 514.5 nm line of an Ar ion laser. The fraction of the crystalline phase to the amorphous phase was evaluated from the transverse optical (TO) phonon signal of the Raman spectra. The crystalline fraction was estimated from an areal ratio of the signal due to the crystalline (c-Si) phase at approximately 521 cm^{-1} to the sum of the signals due to all phase (included the a-Si phase at approximately

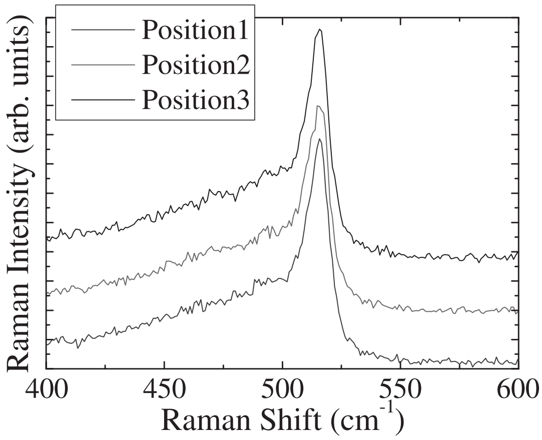


Fig. 1 Raman spectra of sample with a condition of LPX irradiation of 96000 shots followed by IR annealing at 500°C for 30 min. The distance of measured each position is approximately 2 mm.

480 cm^{-1}). The surface morphology of the crystallized film was observed by scanning electron microscopy (SEM) after secco etching. The physical property of a-Si film after LPX irradiation was investigated by spectroscopic ellipsometry and electron spin resonance (ESR), respectively. The spectroscopic ellipsometry measurement was carried out using Xe lamp (beam size of 1.5 mm × 5 mm) at incident angle of 60, 65 and 70°. The measured data was fitted by assuming the film as two layers. The temperature of ESR measurement, the center and range of the magnetic field and power were 10 K, 3367 G, 100 G and 40 μW, respectively.

3. Results and Discussion

Figure 1 shows Raman spectra of sample with a condition of LPX irradiation of 96000 shots followed by IR furnace annealing at 500°C for 30 min. TO phonon peaks are observed at 515 cm^{-1} and the crystalline fraction is 42%. It is found that the crystallization from a-Si occurs although the crystallinity is not enough. Figures 2(a), (b) show the relationships between the crystalline fraction and annealing temperature and between the peak shift, full width at half maximum (FWHM) of TO phonon peak and annealing temperature for the samples with IR furnace annealing and LPX followed by IR furnace annealing, respectively. Although the crystallization temperature by IR furnace annealing without LPX irradiation is 820°C, it reduces down to 420°C by LPX irradiation followed by IR furnace annealing. The threshold temperature of crystallization is reduced by 400°C with a use of LPX irradiation before IR furnace annealing. However, the crystalline fraction for LPX irradiation followed by IR furnace annealing is 40∼50% and that for IR furnace annealing is 80%. The peak shift and the FWHM of TO phonon for the IR furnace annealing with LPX irradiation are larger than those for IR furnace annealing without LPX irradiation. It is thought that the bond angle distortion and lattice relaxation occur enough by LPX irradiation to a-Si film, because the Si bonds are relatively stretchable.[8] The reason why the crystalline fraction decreases, and also the internal stress and defect density of the crystallized film increase for the condition of IR furnace annealing following LPX irradiation is that the low annealing temperature prevents the diffusion of Si atoms following the nucleation. Figures 3(a), (b) show the SEM photographs of the crystallized film after secco etching for the IR furnace annealing at 840°C, 30 min and LPX irradiation for 96000 shots followed by IR furnace annealing at 420°C. The grain was not observed for the sample only irradiated with LPX

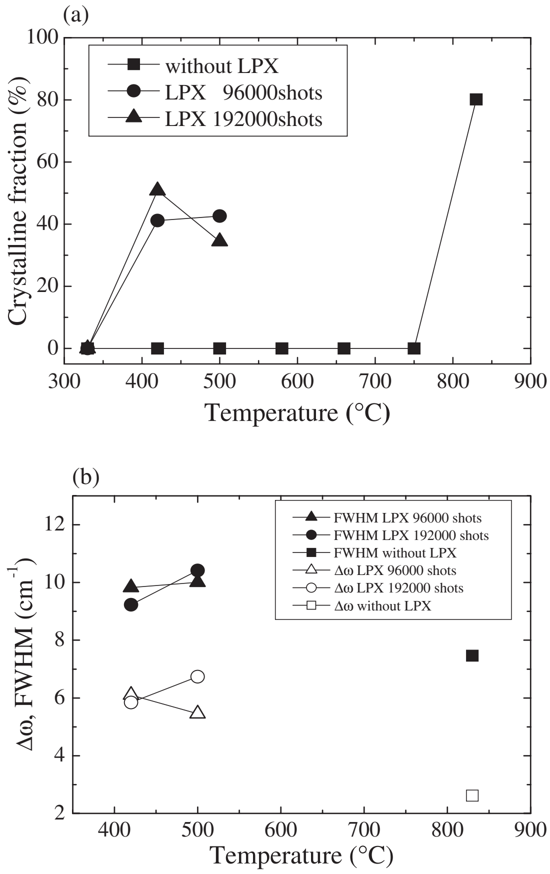
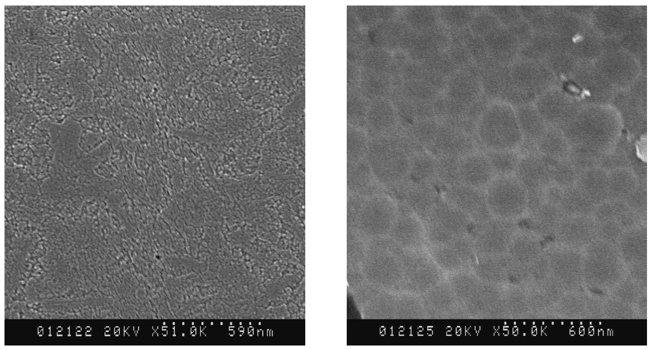


Fig. 2 Relationships between the crystalline fraction and annealing temperature (a) and between the peak shift, full width at half maximum (FWHM) of transverse optical (TO) phonon peak and annealing temperature (b) for the samples with IR furnace annealing and LPX followed by IR furnace annealing, respectively.



(a) IR Furnace Annealing **(b) LPX followed by IR Furnace Annealing**

Fig. 3 SEM photographs of the crystallized film after secco etching for the IR furnace annealing (a) and LPX irradiation followed by IR furnace annealing (b).

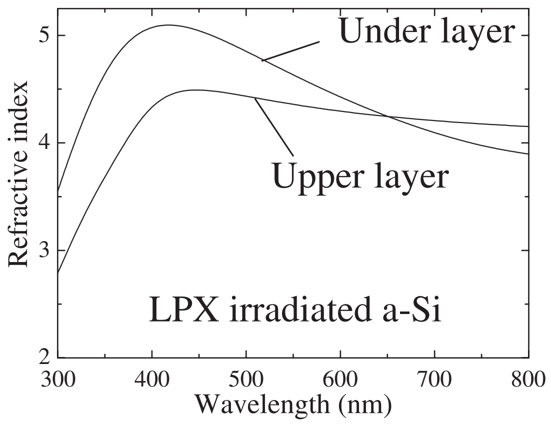


Fig. 4 Relationship between the refractive index and the wave length for the sample with LPX irradiation for 192000 shots. The refractive indexes were calculated from spectroscopic ellipsometry spectra.

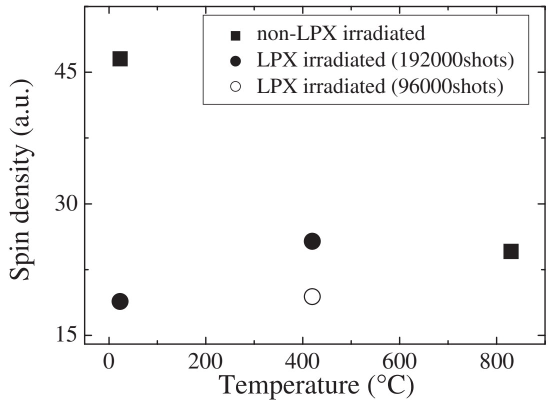


Fig. 5 Dependence of spin densities of as-deposited, LXP-irradiated and annealed a-Si films on anneal temperature.

and also the difference of the surface roughness between these samples before secco etching is thought to be small. The grain sizes for the IR furnace annealing and IR furnace annealing following LPX irradiation are 60 nm and 270 nm, respectively. The nuclei are formed in the vicinity area of the a-Si surface for LPX followed by IR furnace annealing because of the small absorption length of soft X-ray. The density of nuclei is also small for LPX irradiation as discussed later. Next, the characteristic of the a-Si film after LPX irradiation was examined. Figure 4 shows the relationship between the refractive index and the wave length for the sample with LPX irradiation for 192000 shots. The refractive index of upper layer was smaller than that of under layer which is the same as the non-irradiated a-Si film. The thickness of modified layer was estimated to 25 nm. The thickness of SiO_2 on a-Si surface was also estimated from spectroscopic ellipsometry spectra. The SiO_2 thickness of sample irradiated for 96000 and 192000 shots were 5.2 and 9.8 nm, respectively. This thickness was larger than non-irradiated a-Si (2.6 nm). However, we can discuss about the modified layer thickness of a-Si because it was calculated by considering change in the SiO_2 thickness. It is shown that the structural property of a-Si was changed in the vicinity of surface by LPX irradiation.

Figure 5 shows the dependence of spin volume densities of non-irradiated and LPX-irradiated a-Si films on anneal temperature. Dangling-bond density of a-Si with LPX irradiation for 192000 shots was decreased less than $1/2$ in comparison with non-LPX irradiated a-Si. It is considered that the bond angle distortion and the lattice relaxation occur simultaneously. In addition, it is probable that the dehydrogenation[9,10] occurs simultaneously by LPX irradiation. These phenomena influence the diffusion of Si atoms. Consequently, the network of a-Si atoms was reconstructed by remove of dangling bond. The number of dangling bond has hardly changed by annealing after LPX irradiation for 96000 and 192000 shots. It is almost the same as that for annealing at 820°C of non-LPX irradiated sample. These results are understood by considering formation of the quasi-nuclei in a-Si film by the LPX irradiation. LPX irradiation produces the excitation of the L-shell and valence electrons through single-photon absorption. The Si atoms are diffused from the stable site of a-Si bond to the unstable site by the electron excitation via LPX irradiation, and the embryos are formed. Some embryos aggregate and form the quasi-nucleus. Therefore, the density of the quasi-nucleus is small. From the ellipsometry result, the refractive index that is proportional to the packing density decreases approximately 10 percent. If those embryos constituting the quasi-nuclei do not combine with each other, a few dangling-bonds are left at the surface and inside of the quasi-nuclei. By assuming the nano-space as the sphere, the critical radius of the nucleus was calculated using eqs. (1) and (2).

$$\Delta G = -\Delta G_{\rm v}(4/3)(1 - {\rm a}^3)\pi r^3 + \Omega({\rm a}+1)2\pi r^2 \qquad (1)$$

$${\rm d}\Delta G/{\rm d}r = 0 \quad (r = r^*) \qquad (2)$$

Here, ΔG, $\Delta G_{\rm v}$, Ω, r^* are the total free-energy change from a-Si to c-Si, the volume free-energy change from a-Si to c-Si, the surface free-energy of the quasi-nucleus and the critical radius, respectively. Here, assuming the nano-space as the sphere, parameter a (a $\ll 1$) is defined the ratio of the radius of it and the critical radius. It was found that the critical radius $r^*_{\rm QN}$ of the nucleus including the nano-space is given by $r^*_{\rm QN} = \Omega(1+a^2)/\Delta G_{\rm V} = (1+a^2)r^*_{\rm N}$, and $r^*_{\rm QN}$ is a little larger than $r^*_{\rm N}$ non-including the nano-space. It is expected that the large grains are obtained by the LPX irradiation. Figure 6 shows the relationship between the total free energy change per unit volume and crystal grain size in the phase transformation from a-Si to poly-Si by LPX irradiation followed by IR furnace annealing. The free energy increases by LPX irradiation because of the quasi-nucleus formation. The quasi-nucleus transforms to the critical nucleus obtaining the energy difference between the critical nucleus and quasi-nucleus in the IR furnace annealing process.

4. Summary

The crystallization temperature by LPX irradiation followed by IR furnace annealing reduces down to 420°C, although that by IR furnace annealing without LPX irradiation is 820°C. The grain sizes for the IR furnace annealing and IR furnace annealing following LPX irradiation are 60 nm and 270 nm, respectively. This phenomenon is related

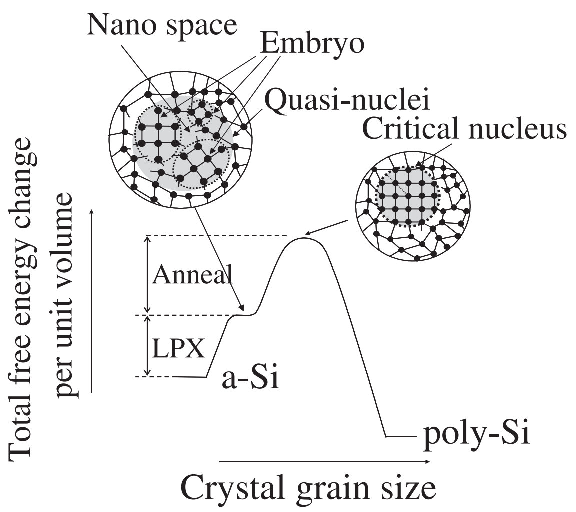


Fig. 6 Relationship between the total free energy per unit volume and grain size in the phase transformation from a-Si to poly-Si by LPX irradiation followed by IR furnace annealing.

with the change in characteristic of a-Si film which is generated by the bond distortion and relaxation during the LPX irradiation. The LPX-irradiated film is constituted by the two different layers. The refractive index of upper layer was lower than that of under layer which is the same as the non-irradiated a-Si film. The dangling bond density of a-Si film was also decreased by LPX irradiation to a-Si film. From these results, the nuclei formation was discussed by considering the quasi-nuclei and embryos which constitute the quasi-nuclei.

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