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Low-temperature Crystallization of a-Si, a-Ge and a-$Si_{1-x}Ge_x$ Films by Soft X-ray Irradiation

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1. Introduction

The low-temperature crystallizations of amorphous semiconductor materials are important for realizing high quality flexible displays and solar cells.

We proposed a low-temperature crystallization method that uses soft X-ray irradiation from the synchrotron radiation facility, NewSUBARU [1-4]. In this study, the effects of soft X-ray irradiation on the structural properties of a-Si, a-Ge and a-SiGe films were investigated for the low-temperature crystallization.

2. Exprimental

An a-Si film was deposited on a glass substrate via plasma-enhanced chemical vapor deposition (PECVD). a-Ge films and a-$Si_{1-x}Ge_x$ films with various Ge fractions (X= 0.2, 0.4, 0.5, 0.6 and 0.8) were deposited on a quartz substrate via molecular beam deposition (MBD). The film thickness was 50 nm. In addition, to apply solar cells, thick a-SiGe film (200nm) with graduated Ge fraction was also prepared by controlling of MBD condition. This sample consists of $Si_{0.8}Ge_{0.2}$ (50nm)/ $Si_{0.6}Ge_{0.4}$ (50nm)/ $Si_{0.4}Ge_{0.6}$ (50nm)/ $Si_{0.2}Ge_{0.8}$ (50nm)/quartz substrate.

The irradiation of soft X-ray was carried out at BL07A of NewSUBARU. The light source of BL07A was a 3-m undulator. The photon energy incident on the sample was controlled via the gap of the undulator. The beam size measured by fluorescent plate on sample surface was 7.5 × 7.5 mm^2. The photon energies were 50, 115 and 130 eV. These photon energies relates to the core level of Ge 3d (29.8 eV), Ge 3p (124.9 eV) and Si 2p (99.8eV). The storage-ring current were varied from 25 to 220 mA. The dose quantity was 50 mA h. The structural properties of the film were measured using Raman scattering spectroscopy.

3. Results and discussion

The crystalline fraction of the Si and Ge films as a function of the sample saturation temperature is shown in Fig. 1. The crystallization temperatures of both the a-Si and a-Ge films began to decrease at about 100 °C.

The dependence of the photon energy on the Raman peak shift and FWHM of irradiated Ge films are shown in Figs. 2 (a) and (b). The Raman peak shift and FWHM were the same for samples irradiated at 50 and 115 eV. However, for photon energies over 130 eV, the Raman peak shift decreased and the FWHM of the peaks increased with increasing photon energy.

The crystalline fraction for the Ge and $Si_{0.5}Ge_{0.5}$ film as a function of storage-ring current is shown in Figs. 3 (a) and (b). For photon energy of 130 eV, both Ge and $Si_{0.5}Ge_{0.5}$ film did not crystallize. This photon-energy dependence can be explained by considering of photoionization cross section and Fermi golden rule.

The crystallization area of $Si_{1-x}Ge_x$ film irradiated at various conditions as a function of Ge fraction is shown in Fig. 4. It is found that crystallization can be occurred at condition of high Ge fraction and high photon flux. The crystallization was enhanced by using a photon energy of 50 eV. It is shown that the photon excitation of Ge atom is effective compared with Si atom for SiGe film.

The optical image, Raman spectra and schematic diagram of crystallization area of Ge fraction graduated sample are shown in Figs. 5, 6 and 7, respectively. Some Raman peaks due to each Ge fraction layer were observed. The crystallization area relates to both photon flux and Ge fraction. The thick a-SiGe film can be crystallized by controlling the Ge fraction and each layer thickness.

The crystallization process is shown in Fig. 8. The atomic migration was enhanced by electron excitation during soft X-ray irradiation. The critical crystallization temperature decreased because of the presence of quasi-nuclei that formed as a result of the soft X-ray irradiation. We believe that low-temperature crystallization can be realized through soft X-ray irradiation techniques.

4. Conclusions

1) With the use of soft X-ray irradiation, the crystallization temperatures of the a-Si and a-Ge films decreased from 680 °C to 580 °C and from 500 °C to 390 °C, respectively.

2) The effects of soft X-ray irradiation on crystallization strongly depend on the excitation of core electrons to vacuum level, resulted in the atom migration.

References

[1] N. Matsuo et al., Dig. AM-LCD, 2005, p.293.
[2] N. Matsuo et al., Jpn. J. Appl. Phys. **46** (2007) 1061.
[3] A. Heya et al., Jpn. J. Appl. Phys. **48** (2009) 050208-1.
[4] N. Matsuo et al., Materials Trans. **51** (2010) 1490.

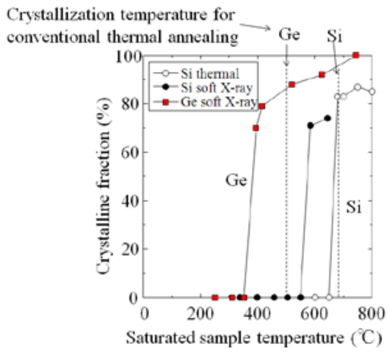

Fig. 1. Crystalline fraction for the Si and Ge films as a function of the sample saturation temperature.

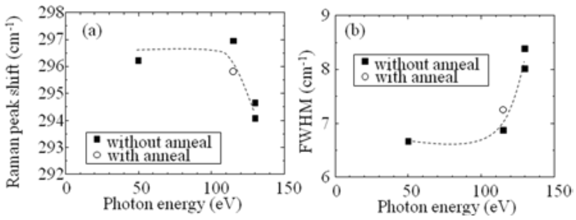

Fig. 2. Dependence of the (a) Raman peak shift and (b) FWHM on the photon energy for a Ge film. The open-circle and closed-square plots represent the Ge films with and without pre-annealing, respectively.

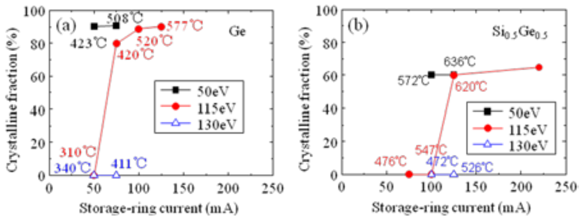

Fig. 3. Crystalline fraction for the Ge and $Si_{0.5}Ge_{0.5}$ film as a function of storage-ring current. (a) Ge film. (b) $Si_{0.5}Ge_{0.5}$ film. For photon energy of 130 eV, both Ge and $Si_{0.5}Ge_{0.5}$ film did not crystallize. The crystallization can occur above threshold photon flux density. The excitation probability of 3d core electrons from core energy level to the vacuum level dominates this phenomenon.

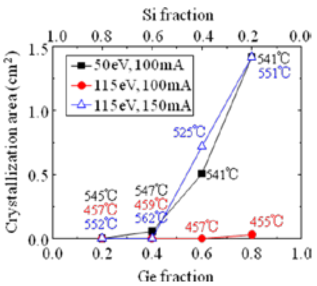

Fig. 4. Crystallization area of SiGe film irradiated at various conditions as a function of Ge fraction. For 115 eV and 100 mA, the crystallization was confirmed at high Ge fraction ($Si_{0.2}Ge_{0.8}$) film. As the storage-ring current increased, the crystallization area increased and crystallization can be occurred at lower Ge fraction film ($Si_{0.4}Ge_{0.6}$ film) by increment of photon flux.

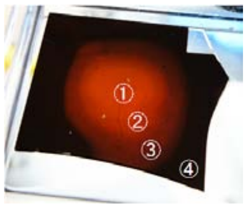

Fig. 5. Optical image of Ge fraction graduated sample. The photon energy and storage-ring current were 50 eV and 100 mA, respectively.

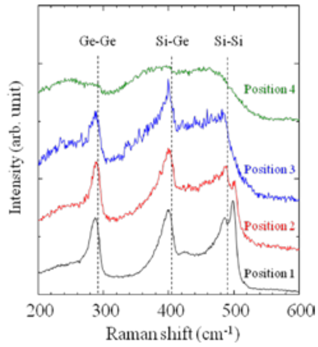

Fig. 6. Raman spectra of Ge fraction graduated sample. Measurement positions are shown in Fig.5. Dashed lines show the peak position for $Si_{0.5}Ge_{0.5}$ film.

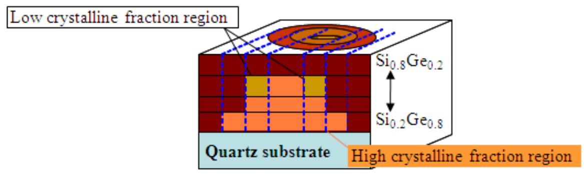

Fig. 7. Schematic diagram of crystallization area of Ge fraction graduated sample. The crystallization area relates to both photon flux and Ge fraction.

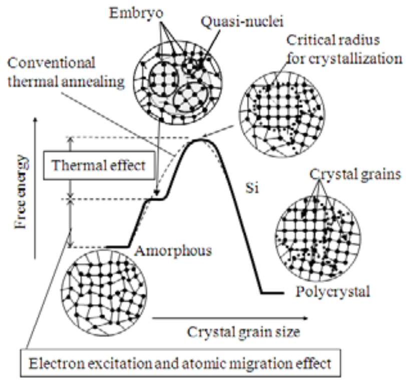

Fig. 8. Crystallization process involving soft X-ray irradiation supplied by the NewSUBARU BL07A facility. The positions of the Si atoms can be shifted by the electron excitations. Consequently, the atoms are locally reordered. We call this region the quasi-nucleus. The quasi-nuclei grew to the critical radius of crystallization via thermal effects. In this case, these crystal grains can be grown without the need for the nucleation energy.