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Soft X-ray Crystallization of $Si_{1-x}Ge_x$ Multilayer Films

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Abstract

Effect of soft X-ray irradiation on the crystallization of a $Si_{1-x}Ge_x$ multilayer film was investigated. The crystallization is influenced by the Ge concentration. The Ge atom was a trigger for the crystallization because the atomic migration of Ge atoms was enhanced by electron excitation during soft X-ray irradiation. For the $Si_{1-x}Ge_x$ multilayer film, the crystallization region can be controlled by the Ge concentration for each layer. The present crystallization technique can be applied to the fabrication of solar cells with high-conversion efficiency.

1. Introduction

Low-temperature crystallizations of amorphous semiconductor materials are important for realizing high-quality solar cells. We proposed a low-temperature crystallization using soft X-ray source [1-4].

In this paper, to realize control of optical absorption and crystallization by Ge concentration, the effects of soft X-ray irradiation on the structural properties of a $Si_{1-x}Ge_x$ multilayer film were investigated by transmission electron microscopy (TEM) observation for high-efficiency solar cells.

2. Experimental

An amorphous multilayer $Si_{0.8}Ge_{0.2}$ (50 nm)/ $Si_{0.6}Ge_{0.4}$ (50 nm)/ $Si_{0.4}Ge_{0.6}$ (50 nm)/ $Si_{0.2}Ge_{0.8}$ (50 nm) film was deposited on a quartz substrate at room temperature by molecular beam deposition.

The irradiation of soft X-ray was carried out at BL07A of NewSUBARU (Fig. 1). The light source of BL07A was a 2.28m-undulator. The irradiated photon energy was 50 eV. This photon energy relate to the core level of Ge 3d (29.8 eV). The storage-ring current and dose quantity were 100 mA and 50 mAh, respectively.

The structural properties were evaluated by Raman scattering and TEM. The depth profiles of Si, Ge, O, and C atoms were obtained using energy dispersive X-ray spectrometry.

3. Results and discussion

The Raman spectra of the $Si_{1-x}Ge_x$ multilayer film at the center of irradiation region are shown in Fig. 2. The Si-Si Raman spectrum can be fitted by three peaks at positions of 501.6, 489.7, and 482.5 cm^{-1} (Fig. 2(b)). These peaks related with the crystalline $Si_{1-x}Ge_x$ layers with Ge concentrations of 0.4, 0.6, and 0.8.

The cross-sectional TEM image and diffraction patterns obtained from each layer of the $Si_{1-x}Ge_x$ multilayer film are shown in Fig. 3. The diffraction patterns of $Si_{0.2}Ge_{0.8}$ and $Si_{0.4}Ge_{0.6}$ layers indicate a single crystalline phase in the selected area. On the other hand, the ring and spot patterns due to the polycrystalline phase were observed in the $Si_{0.6}Ge_{0.4}$ layer. As shown in the Raman spectrum (Fig. 2(b)), it is confirmed that $Si_{0.2}Ge_{0.8}$, $Si_{0.4}Ge_{0.6}$, and $Si_{0.6}Ge_{0.4}$ layers were crystallized. The absorbed photon flux at the upper part is higher than that at the lower part. However, the crystallization occurred only at the lower half part of the layer for the $Si_{0.6}Ge_{0.4}$ layer. Thus, the crystallization of the lower half part of the $Si_{0.6}Ge_{0.4}$ layer was indicated to be enhanced by the crystallization of the $Si_{0.4}Ge_{0.6}$ layer. The depth profiles of Si, Ge, O, and C atoms are shown in Fig. 4. The Ge and Si concentration profiles after the soft X-ray irradiation (crystallization) were identical to those before the irradiation. This suggests that grain growth occurred through the layer interfaces, the Si and Ge concentrations were maintained at the initial concentration.

The high-resolution TEM (HRTEM) images at the interfaces between each layer are shown in Fig. 5. Crystal growth with continuity in crystal orientation through the layer interfaces can be achieved by the soft X-ray crystallization. In addition, the amorphous phase at the interface between the $Si_{0.2}Ge_{0.8}$ layer and the quartz substrate was not observed by HRTEM.

The [112] diffraction pattern obtained in the $Si_{0.2}Ge_{0.8}$ layer is shown in Fig. 6. The SiGe layers have a diamond–lattice based structure. The weak spots due to superstructure reflection or twin were confirmed separately from the diffraction spots of the basic reflection due to the diamond structure in Fig. 6. They suggest that the periodicity of arrangement for Si and Ge atoms along [311] has a twice larger than that of the diamond structure. However, the spots of the superstructure reflection are weak, and there is no compound phase in the Si-Ge binary phase diagram. It is considered that a metastable state with local ordering appeared in the crystallization using soft X-ray irradiation.

Therefore, the superstructure reflection would disappear by enough soft X-ray irradiation and heat treatment.

4. Conclusions

1) Ge concentration is important for the crystallization of a $Si_{1-x}Ge_x$ multilayer film. The Si-Ge concentration in each layer maintained before and after soft X-ray crystallization. Crystal growth with continuity in crystal orientation through the layer interfaces was observed.

2) The local ordering of Si and Ge atoms appeared by soft X-ray irradiation, although the intensity of diffraction spots due to the superstructure reflection or twin is weak.

3) We believe that the crystallization through soft X-ray irradiation techniques can be applied to the fabrication of solar cells with the best optical absorption property.

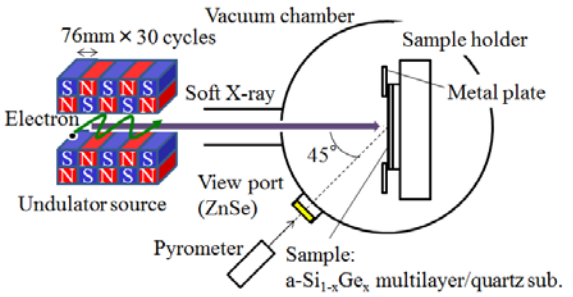

Fig. 1 A schematic diagram of soft X-ray crystallization apparatus. Soft X-ray is generated from a 2.28m-undulator at BL07A in synchrotron facility, NewSUBARU.

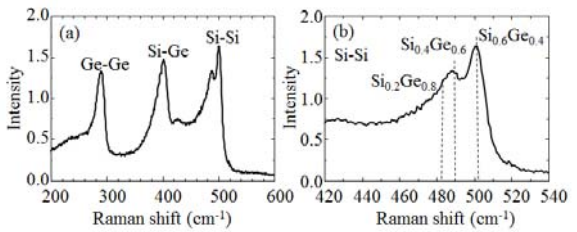

Fig. 2 Raman spectra of the $Si_{1-x}Ge_x$ multilayer film crystallized by soft X-ray irradiation. (a) Raman peaks due to Si-Si, Si-Ge and Ge-Ge bonds. (b) Raman peak of Si-Si bond. Dashed lines show the peak positions of the $Si_{1-x}Ge_x$ (x=0.4, 0.6 and 0.8) layers.

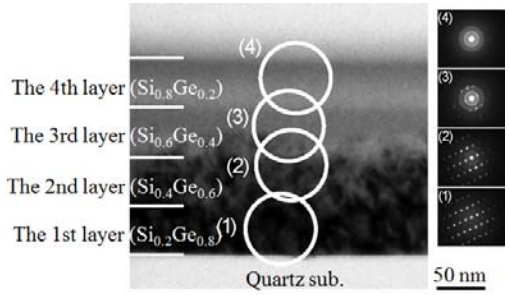

Fig. 3 A cross-sectional TEM image and diffraction patterns from each layer of the $Si_{1-x}Ge_x$ multilayer film irradiated at 50 eV and 100 mA. The 1st, the 2nd and the 3rd layers were crystallized.

References

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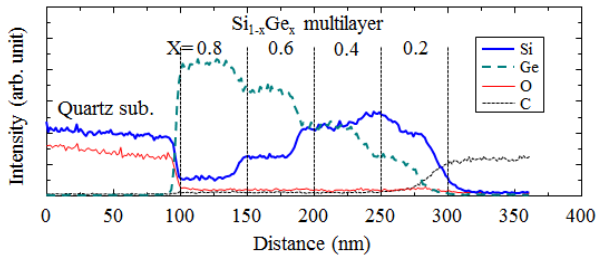

Fig. 4 Depth profiles of Si, Ge, O, and C atoms. The Si-Ge concentration in each layer maintained before and after soft X-ray crystallization.

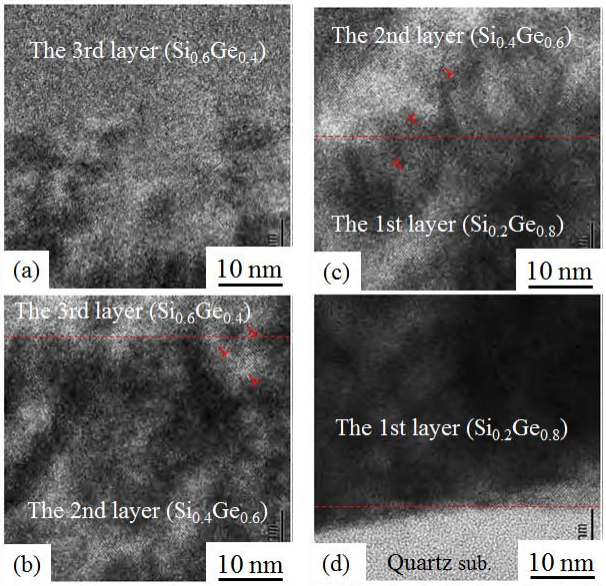

Fig. 5 Cross-sectional HRTEM images at (a) the 3rd layer and at interface between (b) the 3rd and the 2nd layers, (c) the 2nd and the 1st layers, and (d) the 1st layer and a quartz substrate. Observed dislocations show dislocation symbol (⊥). Crystal growth with continuity in crystal orientation through the layer interfaces was observed.

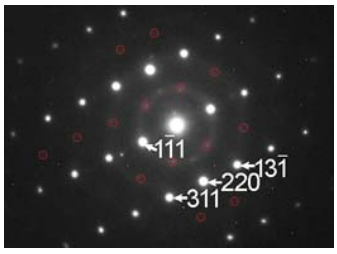

Fig. 6 An electron diffraction pattern of the crystallized $Si_{0.2}Ge_{0.8}$ layer. The red circle shows the superstructure reflection. The periodicity of arrangement for Si and Ge atoms along [311] has a twice larger than that of the diamond structure.