PS-8-3

Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp188-189

Low-temperature Formation of nc-Si in SiO_x by Soft X-ray Irradiation

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Abstract

The low-temperature formation of nanocrystalline Si (nc-Si) in SiO_x is one of key technologies for the realization of high-quality solar cells. We proposed a low-temperature formation method by X-ray. The amorphous Si in SiO_x film was crystallized by atomic migration via electron excitation by soft X-ray irradiation at the photon energy near the core level of Si2p. The nc-Si can be formed by soft X-ray irradiation at low temperature. The size of nc-Si was estimated to 14 nm from the peak position of Raman spectra.

1. Introduction

The nc-Si in SiO_x is very attractive materials of high-quality thin film solar cells. However, it is required to fabricate at low temperature. The effects of electron excitation and atomic migration by soft X-ray from a 2.28m-undulater at synchrotron radiation facility NewSUBARU on amorphous semiconductor film was investigated [1-4]. In this study, we intended to form nc-Si in SiO_x film by soft X-ray irradiation.

2. Experimental

The SiO_x films were deposited on a quartz substrate (18×20×0.5t mm) by a reactive sputtering. The thickness of SiO_x films was 50 nm. The distance between the substrate and Si target was 100 mm. The sputtering rf power was 300 W. The Ar/O_2 gas flow ratio was changed from 8.3/1.7 to 9.4/0.6, the total flow rate was 10 sccm, and the pressure in chamber was 1.0×10^{-3} Torr. The Si/O ratios of the SiO_x films were measured by X-ray photoelectron spectroscopy .

The soft X-ray irradiation was carried out at BL07A in NewSUBARU(Fig.1). The storage-ring energy was 1.0 GeV. The storage-ring currents was 300 mA. The irradiated photon energy on the sample was 115 eV. This photon energy relates to the core level of Si2p. The dose quantity was fixed at 50 mA・h. The sample temperature during soft X-ray irradiation was monitored by pyrometer using emissivity of 0.8.

Formation of crystalline Si (c-Si) in SiO_x film was characterized using Raman scattering spectroscopy. Crystalline fractions of the a-Si phase in SiO_x films was estimated crystal phase ratio to sum of broad amorphous (480 cm^{-1}) and crystal (521 cm^{-1}) phases.

3. Results and discussion

The optical image of the samples after soft X-ray irradiation is shown in Fig.2. The beam size on the sample surface was ϕ 7.5×7.5 mm. The irradiation region of all the sample changed color. The color change is influenced by the transition from amorphous to crystalline phase. It is considered that amorphous Si (a-Si) in the all samples was crystallized by atomic migration via electron excitation by soft X-ray irradiation at the photon energy near the core level of Si2p[4].

The Raman spectra of SiO_x films after soft X-ray irradiation are shown in Fig.3. A broad peak around 480 cm^{-1}, corresponding to a-Si, was observed in the outside of the soft X-ray irradiation region of the sample with the Si/O ratio of 1.23. On the other hand, a sharp peak at 521 cm^{-1}, corresponding to c-Si, was observed in the irradiation region of the same sample. Similar peaks at 521 cm^{-1} were observed in the samples with the Si/O ratio above 0.67, indicating that a-Si in SiO_x films were crystallized.

The crystalline fraction and the Raman intensity as a function of the Si/O ratio is shown in Fig. 4. The crystalline fraction was increased from 0 to 80 % with increasing the Si/O ratio. In the cases of Si/O = 0.5 and 0.55, the crystallization did not occur. It is considered that cohesion of Si atoms did not occur because the distance between the nearest neighbor Si atoms is far for the low Si density films. As the Si density increased, the cohesion of Si atom is enhanced. Therefore, the crystal phase (crystalline fraction) was increased by increment of Si/O ratio. In addition, the Raman intensity was increased with increasing the Si/O ratio. These results indicate that the density of c-Si was increased with increasing the Si/O ratio.

The Raman peak position as a function of a Si/O ratio is shown in Fig. 5. The Raman peak position was almost constant. This indicates that the grain size of c-Si did not increased with increasing the Si/O ratio. The size of c-Si was estimated to 14 nm from the peak position [5], indicating formation of nc-Si.

The full width at half maximum (FWHM) of Raman peaks as a function of a Si/O ratio is shown in Fig. 6. FWHM was increased by increment of a Si/O ratio. It is reported that FWHM is increased by decreasing the size of nc-Si [5]. In addition, FWHM was influenced by the variation of the grain size distribution and the defect density in crystal grain. Therefore, it suggests that as the Si/O ratio increased, the defect density increased for the nc-Si formed by soft X-ray irradiation.

The property of nc-Si in SiO_2 by soft X-ray irradiation differ from the conventional thermal treatment [6]. This difference relates the behavior of Si atoms during nano-crystal formation. For the photon energy of 115 eV, the electrons in Si2p core orbital was preferentially excited by soft X-ray. Therefore, the migration of Si atoms is active compared with O atoms. It is shown that the nc-Si can be formed by soft X-ray irradiation at low temperature.

4. Conclusions

1) The a-Si in SiO_x films crystallized by soft X-ray irradiation, and the size of nc-Si was estimated to 14 nm from the Raman peak position.

2) It is considered that a-Si in SiO_x film was crystallized by atomic migration via electron excitation by soft X-ray irradiation at the photon energy near the core level of Si2p. The nc-Si can be formed by soft X-ray irradiation at low temperature.

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.
[5] M. Nazrul et al., J. Appl. Phys. **98** (2005) 024309.
[6] F. Iacona et al., J. Appl. Phys. **87** (2000) 1295.

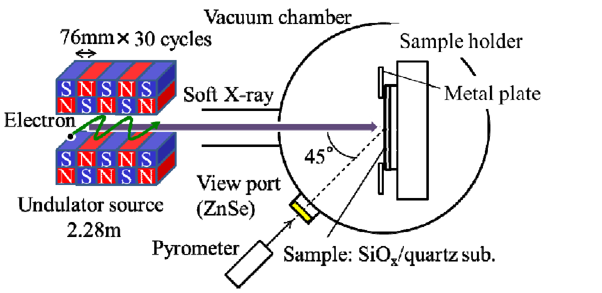

Fig. 1. A schematic diagram of soft X-ray crystallization apparatus. Soft X-ray is generated from a 2.28m-undulator at BL07A in synchrotron facility, NewSUBARU. The sample temperature during soft X-ray irradiation was monitored by pyrometer using emissivity of 0.8. The sample temperatures during soft X-ray irradiation were about 660°C.

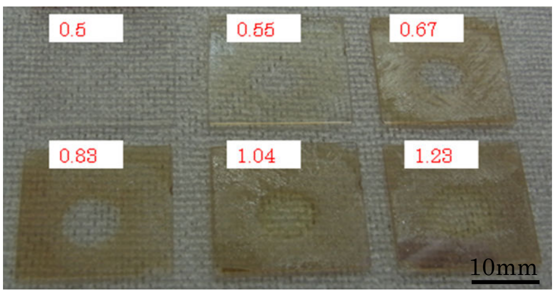

Fig. 2. The optical image of the samples with Si/O ratios between 0.5 and 1.23 after soft X-ray irradiation. Sample color was changed in the center circle, which corresponds to the irradiation region. The color change is influenced by the transition from amorphous to crystalline phase.

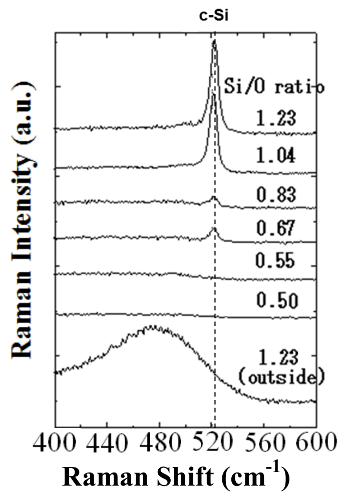

Fig. 3. The Raman spectra of SiO_x films after soft X-ray irradiation The dotted line shows the Raman peak position of c-Si. The a-Si phase in SiO_x films were crystallized in Si/O ratio above 0.67.

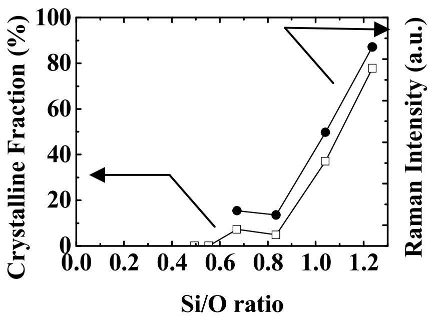

Fig. 4. The crystalline fraction and the Raman intensity of c-Si peak as a function of Si/O ratio in the SiO_x films.

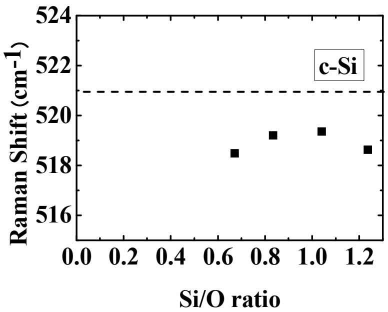

Fig. 5. The Raman peak position as a function of a Si/O ratio. The dotted line shows Raman shift of c-Si. The size of Si nanocrystal was estimated to 14 nm from the peak position.

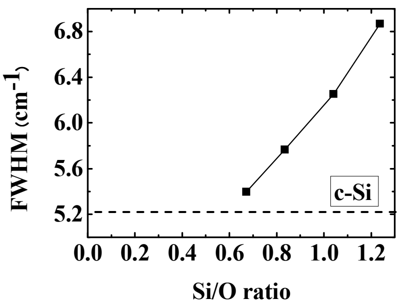

Fig. 6. FWHM of Raman peaks as a function of a Si/O ratio. The dotted line shows FHWM of c-Si.