Thin Solid Films 534 (2013) 334–340

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Low-temperature crystallization of amorphous silicon and amorphous germanium by soft X-ray irradiation

Akira Heya [a,*], Kazuhiro Kanda [b], Kaoru Toko [c], Taizoh Sadoh [c], Sho Amano [b], Naoto Matsuo [a], Shuji Miyamoto [b], Masanobu Miyao [c], Takayasu Mochizuki [b]

[a] Department of Materials Science and Chemistry, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671–2280, Japan
[b] Laboratory of Advanced Science and Technology for Industry (LASTI), University of Hyogo, 3-2-1 Koto, Kamigori, Hyogo 678–1205, Japan
[c] Department of Electronics, Kyushu University, 744 Nishi-ku, Motooka, Fukuoka 819–0395, Japan

ARTICLE INFO

Article history:
Received 9 April 2012
Received in revised form 29 January 2013
Accepted 27 February 2013
Available online 13 March 2013

Keywords:
Soft X-ray irradiation
Crystallization
Amorphous silicon
Amorphous germanium
Nuclei

ABSTRACT

The low-temperature-crystallization effects of soft X-ray irradiation on the structural properties of amorphous Si and amorphous Ge films were investigated. From the differences in crystallization between Si and Ge, it was found that the effects of soft X-ray irradiation on the crystallization strongly depended on the energy band gap and energy level. The crystallization temperatures of the amorphous Si and amorphous Ge films decreased from 953 K to 853 K and 773 K to 663 K, respectively. The decrease in crystallization temperature was also related to atoms transitioning into a quasi-nucleic phase in the films. The ratio of electron excitation and migration effects to thermal effects was controlled using the storage-ring current (photon flux density). Therefore, we believe that low-temperature crystallization can be realized by controlling atomic migration through electron excitation.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The low-temperature crystallization of amorphous silicon (a-Si) and amorphous germanium (a-Ge) is important for the realization of high-quality flexible displays and solar cells. Therefore, low-temperature crystallization methods, including excimer-laser annealing (ELA) [1–3], rapid thermal annealing [4,5], plasma-jet annealing [6,7] and metal-induced lateral crystallization [8], have been widely investigated. To suppress the damage to the glass substrate, most of these methods use liquid crystallization processes that have short durations from sub-microseconds [9,10] to several tens of milliseconds [11]. In addition, the explosive crystallization [12] of amorphous semiconductors was studied for laser irradiation [13] and flash lamp annealing [14].

In the case of thermal crystallization, the thermal energy is necessary to surmount the potential associated with the activation energy of nucleation (E_n) and the crystal grain growth (E_g). It was reported that the E_n and E_g of Si and Ge were 5.3 and 3.1 eV [15], and 3.9 [16] and 2.0 eV [17], respectively. Spinella et al. estimated the E_n and E_g from the nucleation rate and growth velocity as a function of the reciprocal temperature for the annealing of a-Si/SiO_2/c-Si substrate in the range of 853–1053 K [15]. Typically, E_n is large compared with E_g, although the value of the activation energy is changed by the initial properties of the amorphous film, and the treatment conditions. The nucleation requires higher activation energy than the crystal growth. If nucleation is achieved without using thermal energy, the crystallization temperature can be decreased. Therefore, the nucleation process in the absence of thermal energy is important for the realization of low-temperature crystallization.

The effects of hard X-ray (photon energy of 4 keV) irradiation on the thermal crystallization of a-Si [18,19] or a-$Si_{0.98}Ge_{0.02}$ films [20] have been reported, and hard X-ray irradiation from a wiggler has been used to grow dislocation-free silicon films via solid-phase epitaxy of a-Si on a c-Si substrate [18]. In this case, the temperature of the Si film increased to approximately 773 K during the irradiation, in spite of the use of water cooling. To date, hard X-ray sources have not been used for low-temperature crystallization, because the sample temperature becomes very high during hard X-ray irradiation.

We proposed a low-temperature crystallization method that uses soft X-ray irradiation [21] from the synchrotron orbital radiation facility NewSUBARU [22]. We also reported that laser-plasma soft X-ray (LPX) irradiation prior to ELA decreased the critical energy density for crystallization of a-Si film, from 70 to 50 mJ/cm^2 [23,24]. In addition, the required temperature for crystallization via LPX irradiation followed by infrared furnace annealing was reduced from 1103 to 693 K [25]. We believe that the effect of the LPX irradiation on the crystallization originates from the excitation of phonons in the a-Si [24,25].

In this study, the effects of soft X-ray irradiation on the structural properties of a-Si and a-Ge films were investigated using Raman scattering spectroscopy. Based on the differences in crystallization between Si and Ge, we discussed the effects of soft X-ray irradiation on the crystallization and the crystallization mechanisms.

* Corresponding author. Tel.: +81 3 79 267 4909; fax: +81 3 79 267 4885.
E-mail address: heya@eng.u-hyogo.ac.jp (A. Heya).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.02.129

2. Experimental details

An a-Si film was deposited on a SiO_2/glass substrate via plasma-enhanced chemical vapor deposition at 673 K, using Si_2H_6 source gas. The a-Si film thickness was 50 nm, measured using a contact profile meter. The deposition rate and the hydrogen content in the as-deposited a-Si film were 0.2 nm/s and 10 at.%, respectively. The a-Si films were dehydrogenated at 723 K using thermal annealing, and the hydrogen content in the a-Si was below 1 at.%. The hydrogen contents were estimated using Fourier transform infrared measurements [26].

An a-Ge film was deposited on a quartz substrate at room temperature via molecular beam deposition, using a Knudsen cell [27]. The base pressure and deposition rate were 9×10^{-7} Pa and 0.02 nm/s, respectively. Incubation time to start the crystallization exists for the thermal crystallization of Ge films [27]; it was shown that the time needed for crystallization decreased from 3600 to 300 s under pre-thermal annealing at 623 K for 600 s. In this paper, Ge films were deposited using the above-mentioned process; the films were deposited with and without the pre-thermal annealing of the a-Ge films, where the pre-thermal annealing was performed at 623 K for 600 s in vacuum. The thickness of both films was 50 nm. During deposition, the a-Ge film thickness was monitored using a quartz frequency unit.

The soft X-ray irradiation was carried out at the BL07A at NewSUBARU. The light source of BL07A was a 3 m undulator. The undulator light was introduced to the sample stage via a cylindrical mirror. The electron energy of the NewSUBARU ring was 1.0 GeV during this experiment. The irradiation parameters are summarized in Table 1. The photon energy incident on the sample was controlled by changing the gap in the undulator. The photon energies were 50, 115, and 130 eV. The wavelengths of these X-rays were 24.8, 10.8, and 9.53 nm, respectively. The fluence was estimated as 33, 11, and 8.1 J/mm^2 at photon energies of 50, 115, and 130 eV from the photocurrents in the photodiode with a storage-ring current of 220 mA. The X-ray beam size was 7.5×7.5 mm^2, measured using a fluorescent plate on the sample holder. The ambient pressure during irradiation was 5×10^{-5} Pa. For a storage-ring current of 220 mA, the photon flux density on the sample surface was estimated to be 7.3×10^{14} photons/(s mm^2) from the photo current measured using the photodiode. This photon flux density was approximately eighty five times larger than that produced by LPX (8.6×10^{12} photons/(s mm^2) [23]).

The sample temperature was measured using a thermocouple (TC) and a pyrometer, as shown in Fig. 1. The temperature distribution of the a-Si/SiO_2/glass substrate was measured by moving the sample. In this case, a K-type TC was attached to the surface of an a-Si/SiO_2/glass substrate with a size of 10×10 mm^2, via a ceramic bond. Other temperature measurements were performed for storage-ring currents that varied from 25 to 220 mA and a photon energy of 115 eV, using a pyrometer. The emissivity of Si and glass are known to be 0.61 and 0.95, respectively. When the emissivity of the Si film on the quartz substrate was 0.8, the temperature measured using the pyrometer agreed with that measured using the TC. We believe that the pyrometer detected the heat radiation from both the Si film and the glass substrate, because the a-Si film was thin. Because of these results, the sample temperatures were measured using the pyrometer, using an emissivity of 0.8.

To evaluate the difference in the critical value of the crystallization temperature for soft X-ray irradiation and thermal annealing, a-Si films were annealed at 873, 923, 953, 973, 1023, and 1073 K in an infrared furnace, as a reference. The sample temperature was measured using a TC attached to the a-Si/SiO_2/glass substrate, similar to the temperature measurements performed during soft X-ray irradiation. In addition, a-Ge films were also annealed at 673, 723, and 773 K in an infrared furnace.

Table 1
Soft X-ray irradiation parameters for a-Si and a-Ge.

Condition	A	B	C	D
Sample	a-Si	a-Si	a-Ge	a-Ge
Photon energy (eV)	115	115	50, 115, 130	115
Photon wavelength (nm)	10.8	10.8	24.5, 10.8, 9.53	10.8
Dose (mA h)	3 - 500	50	50	50
Storage-ring current (mA)	220	25 - 220	220	25 - 220

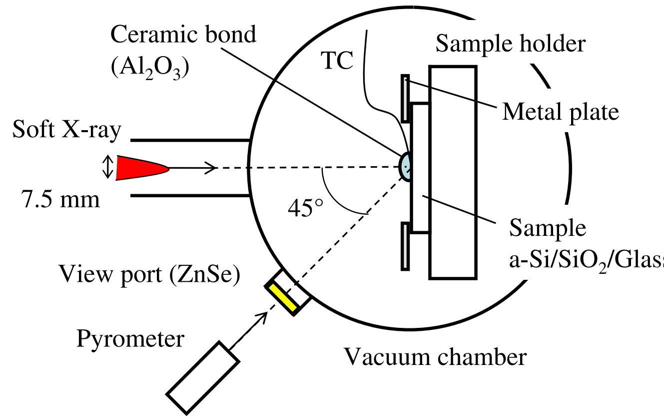

Fig. 1. Setup for measuring the sample temperature using a TC and a pyrometer.

The changes in the structural properties of the film were measured using Raman scattering spectroscopy. The Raman spectroscopy was carried out at room temperature using the 514.5 nm line from an Ar-ion laser. The measurement region for the Raman spectroscopy was a few micrometer in diameter in the plane, and a few μm in depth. Raman spectra were obtained at the center of the irradiation and non-irradiation areas. The horizontal axis (wave number) in the Raman spectrum was corrected using the 521 cm^{-1} peak position for a single-crystal Si substrate, measured before and after the sample measurements. The ratio of the crystalline and amorphous phases was evaluated using the transverse optical phonon signal of the Raman spectra. For the Si film, the crystalline fraction was estimated using the ratio of the signal from the crystalline phase at approximately 521 cm^{-1} [28] to the sum of the signals from both the crystalline and amorphous phases at approximately 480 cm^{-1}. However, the peaks originating from the crystalline and amorphous phases of the Ge film were at 300 [29] and 270 cm^{-1}, respectively.

3. Results and discussion

3.1. Sample temperature during soft X-ray irradiation

The temperature distribution on the a-Si film/SiO_2/glass substrate is shown in Fig. 2. The maximum and minimum temperatures were 953 and 613 K, respectively. The difference in temperature was large, despite the small sample sizes, because the soft X-ray beam was small and the thermal conductivity of the glass substrate was low. For LPX irradiation, the temperature of the a-Si film/glass substrate was 388 K [23]. The sample temperature recorded at NewSUBARU was higher than that at LPX, because of the large photon flux density achieved at NewSUBARU (85×). The maximum temperature was similar to the crystallization temperature needed for conventional furnace annealing. To realize a low-temperature treatment method, it was therefore necessary to decrease the sample temperature by decreasing the storage-ring current.

The relationship between the storage-ring current and the saturated sample temperature of the Si and Ge films is shown in Fig. 3. The sample temperatures in this figure were at a maximum in the center of the soft X-ray irradiation region. The photon flux density on the sample surface was proportional to the storage-ring current. The sample temperature decreased with decreasing storage-ring current. The temperature of

Download English Version:

https://daneshyari.com/en/article/1666292

Download Persian Version:

https://daneshyari.com/article/1666292

Daneshyari.com