doi:10.1017/S1431927617010893
Microsc. Microanal. 23 (Suppl 1), 2017
© Microscopy Society of America 2017

Crystallization Processes of Amorphous GeSn Thin Films by Heat Treatment and Electron Beam Irradiation

T. Kimura[1], M. Ishimaru[1], M. Okugawa[2], R. Nakamura[2] and H. Yasuda[3]

[1.] Department of Materials Science and Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka 804-8550, Japan
[2.] Department of Materials Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
[3.] Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Ibaraki, Osaka 567-0047, Japan

Germanium-tin (GeSn) is anticipated as a component of high-efficiency thin film solar cells, because of its tunable band gap and lattice parameter by changing Sn concentration [1]. For the application, it is necessary to control the Sn concentration in wide range. However, the solubility limit of Sn in Ge matrix is very small, and therefore Sn segregation easily occurs during heat treatment. Recrystallization from amorphous is one of the possible ways to enhance Sn concentration. In fact, GeSn with 25 at%Sn was obtained by thermal annealing at 70 ºC [2]. Low temperature annealing can suppress diffusion of Sn. The synthesis of materials using radiation fields is useful to realize nonequilibrium materials at room temperature. The purpose of this study is to examine crystallization process of amorphous GeSn under heat treatment and electron beam irradiation by transmission electron microscopy (TEM).

Amorphous GeSn thin films were prepared by radio frequency magnetron sputtering method. The Sn chip was placed on the Ge target, and the Sn concentration was controlled by changing the number of chips. Figure 1 shows the sample preparation procedure for TEM observations. The thin film was deposited on a NaCl substrate. The substrate was dissolved by water, and the separated thin film was scooped with a Mo grid. Structural changes during heat treatment and electron beam irradiation were examined by *in situ* TEM observations.

Figure 2 shows a high-resolution TEM (HRTEM) image and the corresponding electron diffraction patterns of as-sputtered specimen prepared by placing 30 Sn chips on a Ge target. The HRTEM image reveals a typical salt and pepper contrast and halo rings appear in the diffraction pattern, indicating that this specimen is amorphous and no remarkable phase separation occurs.

Figure 3 shows electron diffraction patterns as a function of annealing temperature: (a-c) heating process and (d-f) cooling one. From the EDX analysis, the Sn concentration was estimated to 9.7 at%. The amorphous structure was maintained up to 375 ºC, but it was found that crystallization started at 400 ºC (Fig. 3(b)). Finally, complete recrystallization occurs at 500 ºC. It should be noted that only the ring pattern due to the diamond structure appears in Fig. 3(c). This feature remains at 150 ºC during cooling process (Fig. 3(d)), while addition reflections due to β-Sn appear at 100 ºC (Fig. 3(e)). The precipitation temperature of Sn observed here is much lower than the melting point of Sn (~230 ºC). It is reported that the melting point depression occurs depending on particle size [3]. Based on this result, we think the melting point depression is due to the formation of nano-sized Sn particles.

Figure 4 shows the bright field image and the electron diffraction pattern of the specimen with 20.1 at%Sn after electron-beam irradiation. The specimen was irradiated with 125 keV electrons at a flux of 0.15 nA/sec for 3 min at room temperature. It was found that the specimen is completely recrystallized.

https://doi.org/10.1017/S1431927617010893 Published online by Cambridge University Press

In the diffraction pattern, only the Debye-Scherrer rings of the diamond structure was observed. Although the Sn concentration is higher than the heat treated sample (Fig. 3), the Sn precipitation is suppressed in this specimen. This suggests that electron beam irradiation can realize crystalline Ge with high concentration Sn at room temperature. The structural changes of materials under radiation environment are induced by two mechanisms: one is knock-on effect and the other is electron excitation one. When the energy of incident electrons is larger than the displacement energy of the target material, the knock-on effect becomes more pronounced. The knock-on energy, E_{max}, is equal to 4.2eV under the present irradiator conditions (*i.e.*, E = 125 kV). This value is smaller than the displacement energy required for the crystallization of amorphous Ge (7.2 eV) [4], and therefore crystallization mechanism in the present study is attributed to the electron excitation effect.

In conclusion, the thermally-induced and electron beam irradiation-induced crystallization of amorphous GeSn was investigated by *in situ* TEM. Sn segregation occurred in 9.7 at%Sn specimen during heat treatment, whereas no Sn segregation was observed in 20.1 at%Sn specimen crystallized by electron beam irradiation at room temperature. This suggests that electron-beam-irradiation techniques is useful for realizing the low-temperature synthesis of crystalline Ge with high concentration Sn.

References:

[1] S. Zaima *et al*., Sci. Technol. Adv. Mater. **16** (2015) 043502.
[2] K. Toko *et al*., Appl. Phys. Lett. **106** (2015) 082109.
[3] J.-G. Lee and H. Mori, Thin Solid Films **546** (2013) 453.
[4] I. Jencic, I.M. Robertson and J. Skvarc, Nucl. Instr. Meth. Phys. Res. B **148** (1999) 345.

Figure 1. Sample preparation procedure for TEM observations.

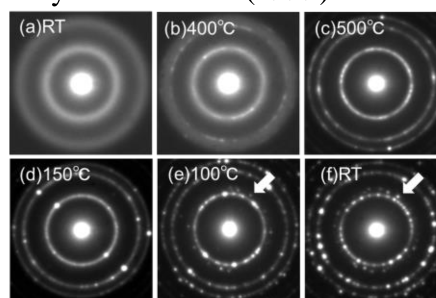

Figure 3. Electron diffraction patterns of 9.7 at%Sn specimen during heat treatment.

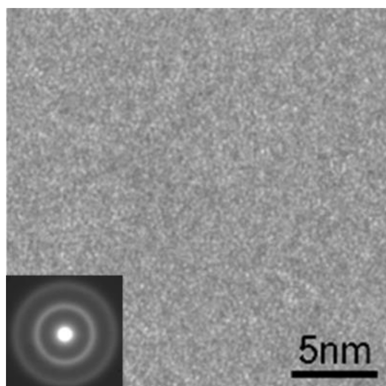

Figure 2. HRTEM image and the corresponding electron diffraction pattern of as-sputtered specimen with 20.1 at%Sn.

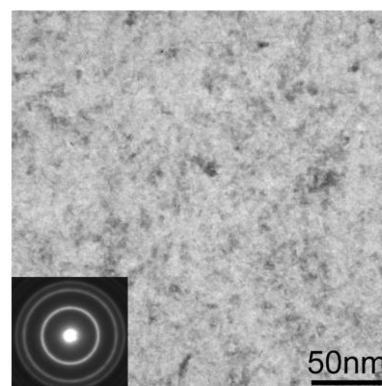

Figure 4. Bright field image and the electron diffraction pattern of 20.1at%Sn specimen after irradiation.

https://doi.org/10.1017/S1431927617010893 Published online by Cambridge University Press