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SYNTHESIS OF HIGH Sn CONCENTRATION GeSn BY RECRYSTALLIZATION OF AMORPHOUS PHASE

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Abstract

Amorphous structures of germanium-tin (GeSn) thin films as well as their recrystallization processes during thermal annealing were examined by means of transmission electron microscopy. The specimens were prepared by radio-frequency magnetron sputtering. The as-sputtered GeSn thin films possessed an amorphous structure with 16.4 at.%Sn. The specimen crystallized at 325 °C, and Sn atoms were substitutionally incorporated in a diamond structure. The Sn atoms were ejected from Ge at 350 °C, and molten Sn were formed. In the cooling process, it was confirmed that the molten Sn remained at 150 ºC which is much lower than the eutectic temperature of the Ge-Sn binary system. Finally, a remarkable Sn precipitates were formed at room temperature.

Introduction

GeSn possesses a higher carrier mobility than Si and Ge, and therefore it is applicable as a channel material for high performance thin film transistors [1]. In addition, the current Si manufacturing processes are easily applied for GeSn, since it consists of the same group-IV element as Si. Because of these, GeSn is anticipated as one of the post-Si materials. To control the physical properties of GeSn, it is necessary to control the Sn concentration in a wide range. However, the solubility limit of Sn in Ge matrix is very small (~1 at.%Sn), and therefore Sn segregation easily occurs during heat treatments.

Much effort has been devoted to enhance Sn concentration in Ge matrix. Recrystallization from amorphous is one of the possible ways to realize high Sn concentration GeSn. In fact, polycrystalline GeSn with 25 at.%Sn was realized by thermal annealing at 70 ºC for 100 hr [2]. To obtain crystalline GeSn from an amorphous phase, it is necessary to control the crystallization processes. However, the details of the crystallization processes are not clear. The purpose of this study is to examine crystallization processes of amorphous GeSn under heat treatment by *in situ* transmission electron microscopy (TEM).

Experimental

The specimens were prepared by the same procedures as described elsewhere [3]. Figure 1 shows a schematic diagram of the radio-frequency magnetron sputtering apparatus and the target. Amorphous GeSn thin films with a thickness of 40 nm were prepared by sputtering at a base pressure of 3×10^{-5} Pa (Fig. 1(a)). Square Sn chips of 5×5 mm^2 were placed on a Ge target with a diameter of 101.6 mm, and the Sn concentration was controlled by changing the number of chips (Fig. 1(b)). The GeSn thin films were deposited on a cleaved NaCl substrate at ambient temperature. The substrate was dissolved by distilled water, and then the separated thin film was recovered on a molybdenum grid.

The specimens were observed by a JEOL JEM-3000F TEM (operated at 300 kV). The Sn concentration of as-sputtered amorphous GeSn was estimated by a quantitative analysis of energy-dispersive x-ray spectra. To examine the thermally-induced structural changes, the specimens were annealed in a TEM using a heating holder. Electron diffraction patterns were recorded on an imaging plate (Eu^{2+}-doped BaFBr) which has higher sensitivity, wider dynamic range, and better linearity for electron-beam intensities compared with the commercial TEM film material. The intensities of halo patterns were digitized quantitatively using an imaging plate processor, DITABIS Micron.

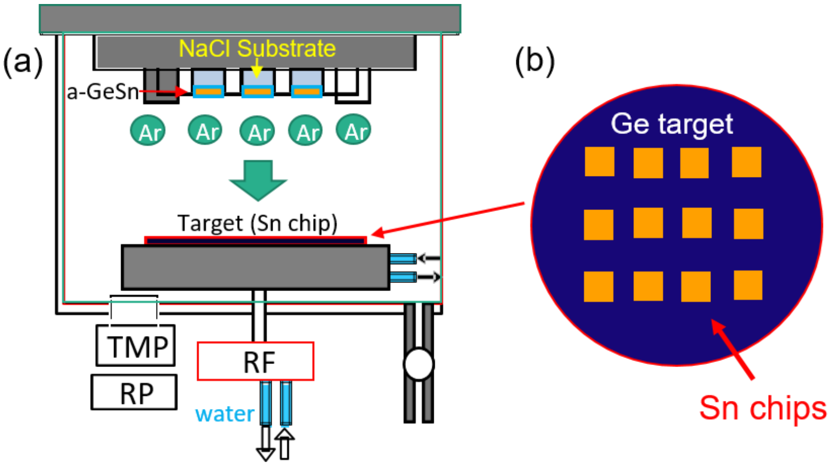

Figure 1. Schematic diagrams of (a) RF magnetron sputtering apparatus and (b) Ge-Sn target. Amorphous GeSn thin films were deposited on cleaved NaCl substrates.

Results and Discussion

Structure Analysis of As-sputtered GeSn

Figure 2(a) shows a high-resolution TEM image and selected-area electron diffraction pattern of the as-sputtered specimen with 16.4 at.%Sn. The image reveals a typical maze contrast and halo rings appear in the diffraction pattern, indicating that this specimen is amorphous. Figure 2(b) shows an atomic pair-distribution function, $g(r)$, of the corresponding specimen. Prominent first and second peaks exist at ~0.25 and ~0.41 nm, respectively, whereas the $g(r)$ converges to unity at the longer distance side. This result is consistent with the feature of amorphous structures. A magnified picture around the first peak of $g(r)$ is shown in Fig. 2(c). Arrows on the horizontal axis denote the first nearest neighbor distance of Ge-Ge, Ge-Sn, and Sn-Sn atomic pairs in a diamond structure. It is apparent that the first main peak exists at 0.247 nm, indicating that the Ge-Ge atomic pairs is predominantly formed in the first nearest neighbor. It should be noted that a shoulder is observed around 0.262 nm which is attributed to the formation of Ge-Sn atomic pairs. This means that the Ge and Sn atoms were mixed within the first coordination shell, and no remarkable phase separation was detected.

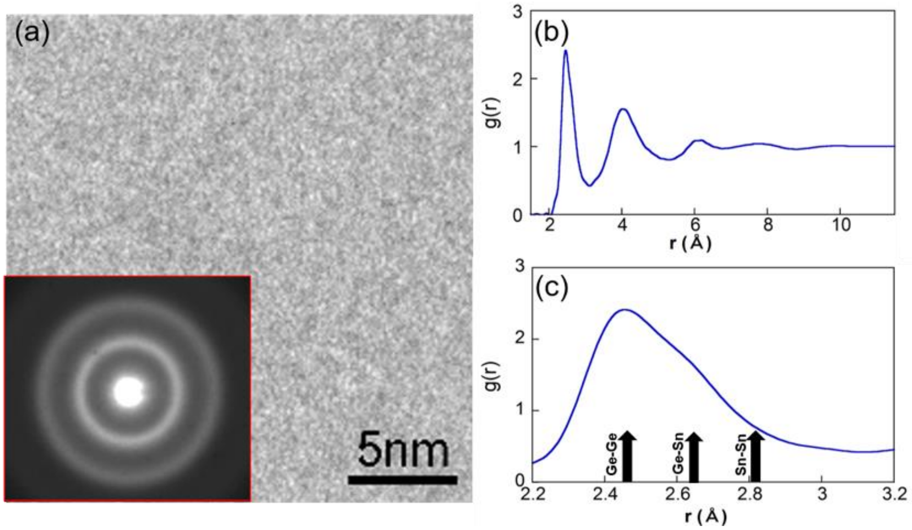

Figure 2. (a) High-resolution TEM image and selected-area electron diffraction pattern of as-sputtered amorphous GeSn with 16.4 at.%Sn. (b) Atomic pair-distribution function and (c) its magnified picture around the first peak.

Thermally-induced Structural Changes

Thermally-induced structural changes of amorphous GeSn were examined by *in situ* TEM. Figure 3 shows the changes of bright-field TEM images and selected-area electron diffraction patterns as a function of annealing temperature: (a) 300 ºC, (b) 325 ºC, and (c) 350 ºC. No remarkable diffraction contrast is observed in the bright-field image of Fig. 3(a) and halo rings exist in the diffraction pattern, indicating that the amorphous structure is maintained up to 300 ºC. The halo rings transform to the Debye-Scherrer rings at 325 ºC (Fig. 3(b)), indicating that crystallization starts at this temperature. We have recently found that GeSn with 9.7 at% Sn crystallizes at 400 °C [3]: the crystallization temperature decreases with increasing the Sn concentration. This is attributed to the metal induced crystallization.

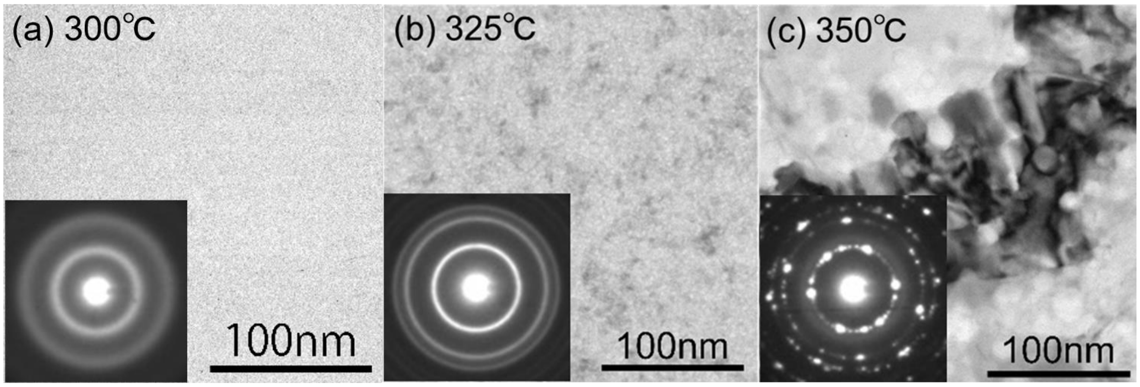

Figure 3. *In situ* TEM observations of structural evolution during heat treatment of 16.4 at% Sn as-sputtered sample: (a) 300 ºC, (b) 325 ºC, and (c) 350 ºC.

The rings can be indexed from the inside as 111, 220, and 311 of a diamond structure, and no extra reflections associated with the secondary phase were observed: Sn atoms are substitutionally incorporated in Ge with a diamond structure. The bright-field TEM image shows that the grain size is several nanometer. On the other hand, the formation of the grains with a size of >100 nm was confirmed in the specimen annealed at 350 ºC (Fig. 3(c)). It should be noted that a halo ring is observed just outside of the 111 Bragg spots due to crystalline GeSn. This is attributed to the formation of molten Sn.

Figure 4 shows the electron diffraction pattern during the cooling process. In addition to the Bragg spots of the diamond structure, a halo ring due to molten Sn is observed at 200 ºC (Fig. 4(a)). The eutectic temperature of the Ge-Sn binary system is ~230 ºC, and therefore the molten Sn is in a supercooled state. The molten Sn presumably disperses in the nanoscale, and it is thought to induce the melting temperature depression. The Sn remains in the liquid state at 150 ºC, but Bragg spots appear in the vicinity of the 111 ring (Fig. 4(b)). This indicates the formation of crystalline β-Sn. From the electron diffraction pattern at room temperature, it can be confirmed that numerous Sn crystallites are precipitated (Fig. 4(c)).

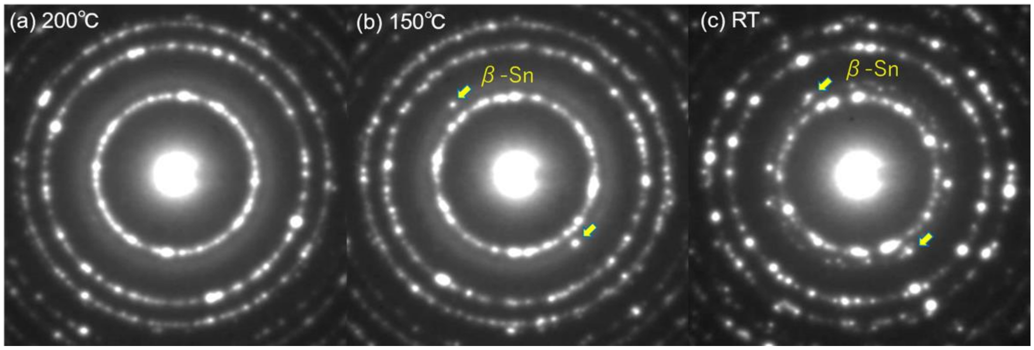

Figure 4. Changes of electron diffraction pattern during cooling process of the specimen with 16.4 at% Sn in the as-sputtered state.

It was found that Sn atoms were successfully incorporated in Ge with a diamond structure just after the crystallization, while the Sn segregation occurs with further annealing at higher temperature. Based on this result, it is considered that thermal annealing at or just below the crystallization temperature is useful to suppress the Sn precipitates. More extensive study is currently underway.

References

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