Formation of Mg$_{2}$Si$_{1-x}$Sn$_{x}$ Thin Films by Co-sputtering and Investigation of their p-type Electrical Conduction

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(Received September 30, 2019)

We obtained Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films on the c-plane sapphire and the (100) CaF$_{2}$ substrates using the radio frequency (RF) magnetron co-sputtering method under various sputtering area ratio of Mg chips to Mg$_{2}$Si (Sn) target and a subsequent two-step annealing process up to 400$^\circ$C. The X-ray diffraction (XRD) and energy-dispersive X-ray spectrometry (EDS) analysis of the samples confirmed that the obtained films were ternary Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films with a composition of x ≈ 0.31. Optical microscopy and EDS mapping images of Mg$_{2}$Si and Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films after annealing at 400$^\circ$C showed remarkable Mg desorption from Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films, but not from Mg$_{2}$Si films. The Hall effect measurements revealed that all Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films annealed at 400$^\circ$C had a p-type conductivity. The first-principles calculations suggested that a combination of two different types of defects, Sn substitution at Si site (Sn$_{Si}$) and Mg vacancy (V$_{Mg}$), which acts as an acceptor, could be the origin of the p-type conductivity of Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films.

1. Introduction

Mg$_{2}$Si is an environmentally friendly material with an indirect bandgap that ranges from 0.6 to 0.8 eV [1-5]. The dimensionless figure of merit (ZT) of Mg$_{2}$Si is known to be high in the 500 K to 800 K range [6] and thus its application in thermoelectric conversion devices is expected. However, since Mg$_{2}$Si has high thermal conductivity, it is necessary to increase phonon scattering to decrease the thermal conductivity of Mg$_{2}$Si [7-11]. One possible way to decrease the thermal conductivity is by adding a third element (Sn) with a large atomic mass to Mg$_{2}$Si. On the other hand, in the phase diagram of Mg$_{2}$Si$_{1-x}$Sn$_{x}$, the mixed-phase of Mg$_{2}$Si and Mg$_{2}$Sn is obtained in the composition range of 0.4 ≤ x ≤ 0.6 due to the presence of miscibility gaps [12]. However, it has been difficult to obtain a ternary solid solution of Mg$_{2}$Si$_{1-x}$Sn$_{x}$ (0.4 ≤ x ≤ 0.6), especially by the crystal growth from the melt due to the large difference in the molecular mass of Mg$_{2}$Si and Mg$_{2}$Sn. There is a report on Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films (0.4 ≤ x ≤ 0.6) formed by co-sputtering using the three elemental targets of Si, Sn and Mg, and they have shown an n-type conductivity with an electron density in the order of $10^{18}$ cm$^{-3}$ [13]. In our previous study, we succeeded in obtaining ternary Mg$_{2}$Si$_{1-x}$Sn$_{x}$ (0 < x < 0.5, 2 > y > 1) films, but all the samples exhibited p-type conductivity, probably due to the presence of Mg vacancy (V$_{Mg}$) [14-15]. The purpose of this study is to clarify the origin of p-type conductivity. We optimized the chemical composition of Mg in single-phase Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films during co-sputtering of Mg$_{2}$Si, Sn and Mg. The relationship between the type of electrical conductivity and the formation energy of the Mg$_{2}$Si$_{1-x}$Sn$_{x}$ crystals containing a few types of point defects was also evaluated by first-principles calculation.

2. Experimental Procedures

2.1 Formation and characterization of Mg$_{2}$Si$_{1-x}$Sn$_{x}$ films
Four Sn chips (3N, 10 × 10 × 1 mm) and various numbers of Mg chips (6N, 5 × 5 × 1 mm) were placed together on a Mg$_2$Si target (3N, φ4 inch × t4.5 mm). The sputtering area ratio of the Mg chips to Mg$_2$Si (Sn) target is defined as Mg/Mg$_2$Si (Sn), and this ratio was varied from 0.0031–0.032. Two types of single side polished substrates were used in this study: one is a c-plan sapphire substrate (φ2 inches × t425 μm) for preforming X-ray diffraction (XRD), optical microscopy, and Hall effect measurements; the other is a (100) CaF$_2$ substrate (10 × 10 × t0.5 mm) for performing scanning electron microscope (SEM)/ energy-dispersive X-ray spectrometry (EDS) analysis. No surface treatment was performed for the two types of as-received substrates before deposition. The deposition chamber was evacuated to $4 \times 10^{-5}$ Pa before starting the sputtering process. Pre-sputtering was performed for 10 min to clean the surfaces of the Mg$_2$Si target as well as the Sn and Mg chips before deposition by sputtering. The Mg$_2$Si$_{1-x}$Sn$_x$ films with a thickness of 300–400 nm were deposited on the c-plane sapphire substrates and the (100) CaF$_2$ substrates by RF magnetron co-sputtering in Ar atmosphere. The deposition working pressure was maintained at 5 Pa. After the deposition, the samples were subjected to two-step annealing in constant Ar (97%)/H$_2$ (3%) flow of 200 sccm: The first step was performed at 200°C for 30 min to remove water remaining in the quartz tube of annealing system, and the second step was performed at 400°C for 30 min to form Mg$_2$Si$_{1-x}$Sn$_x$ films. After annealing, the ohmic electrodes were formed by soldering four indium dots of about φ1 mm at the four corners on the top surface of Mg$_2$Si$_{1-x}$Sn$_x$ films, and the Hall effect measurement was performed at room temperature. The structural properties of the samples were characterized by XRD, optical microscopy, and SEM/ EDS analysis.

2.2 First-principles calculation

First-principles calculations combining density function theory and the projector augmented wave method were performed to investigate the electronic structures of the Mg$_2$Si$_{1-x}$Sn$_x$ crystals, which contain point defects such as Mg vacancy (V$_{Mg}$) and Sn substitution at Si site (Sn$_{Si}$), using the software PHASE/0 (ASMS Co., Ltd.). We employed the generalized gradient approximation method proposed by Perdew-Burke-Ernzerhof (GGA-PBE) to deal with the exchange-correlation energy. The planewave cutoff energies used for the wavefunctions and charge densities were 340 and 3060 eV, respectively. The Brillouin zone (BZ) integration was performed using the tetrahedron method. Periodic boundary conditions were applied along the three lattice vectors. For the k-point sampling of numerical BZ integration, we used a $4 \times 4 \times 4$ mesh for the $3 \times 3 \times 3$ supercell (81 atoms in total). The energetic convergence threshold for the self-consistent field was $2.72 \times 10^{-6}$ eV. The convergence condition for structural optimization was $2.6 \times 10^{-2}$ eVÅ$^{-1}$. The Mg$_2$Si Crystallographic Information File (Mg$_2$Si coordinate and crystal structure), which can be downloaded from the material project database [16], was used to perform calculations.

3. Results and Discussions

3.1 Structural properties

Figure 1 shows the Mg/Mg$_2$Si (Sn) dependence of the XRD spectra for Mg$_2$Si$_{1-x}$Sn$_x$ thin films formed on the c-plane sapphire substrates. From Fig. 1, all the peaks were observed between Mg$_2$Sn and Mg$_2$Si peaks, which indicates a formation of ternary Mg$_2$Si$_{1-x}$Sn$_x$ films. As the Mg content increases, no significant change in the positions of the peaks was observed. Furthermore, no Mg or MgO peaks were observed. The composition ratio of x in Mg$_2$Si$_{1-x}$Sn$_x$ was estimated using Vegard’s law, and it was determined to be 0.31 (i.e., Mg$_2$Si$_{0.69}$Sn$_{0.31}$) at Mg/Mg$_2$Si (Sn) = 0.012.

Figure 2 shows the optical microscope images of the surface of Mg$_2$Si and Mg$_2$Si$_{0.69}$Sn$_{0.31}$ films deposited on c-plane sapphire substrates before and after annealing. Before annealing, both films showed smooth surface morphology. After annealing at 400°C, surface voids were observed for the
Mg$_2$Si$_{0.69}$Sn$_{0.31}$ films, but not for the Mg$_2$Si films. As for the Mg$_2$Si$_{1-x}$Sn$_x$, films with Mg/Mg$_2$Si (Sn) = 0.0031 and 0.0062, no surface voids were observed, but they were observed for the Mg$_2$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012 and 0.032.

EDS mapping analysis was performed to map out the lateral distribution of the elements of the rough surface area with surface voids for the Mg$_2$Si$_{0.69}$Sn$_{0.31}$ films, while the EDS analysis was performed to determine the elemental composition of individual points of the smooth surface area without any surface voids for the Mg$_2$Si$_{1-x}$Sn$_x$ films as a function of Mg/Mg$_2$Si (Sn). It should be noted that the smooth area partially remained in the Mg$_2$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012 and 0.032. CaF$_2$ substrates were used for EDS measurements since CaF$_2$ does not contain elemental oxygen and the constituent elements of the Mg$_2$Si$_{1-x}$Sn$_x$ films.

Figure 3 shows the EDS mapping images of Mg, Si and Sn measured on the rough surface area for the Mg$_2$Si$_{0.69}$Sn$_{0.31}$ (Mg/Mg$_2$Si (Sn) = 0.012) films deposited on the (100) CaF$_2$ substrates after annealing at 400°C. Desorption of Mg, Si, and Sn atoms can be seen from the EDS mapping. This kind of desorption was also observed for films with Mg/Mg$_2$Si (Sn) = 0.032 (data not shown here). For the Mg$_2$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012 and 0.032, the rough surface area occupied about 50% and over 90% of the whole surface area, respectively. Table I shows the chemical composition ratio of Mg$_2$Si$_{1-x}$Sn$_x$ films deposited on the (100) CaF$_2$ substrates with Mg/Mg$_2$Si (Sn) = 0.012 before and after annealing. As for the annealed Mg$_2$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012, two points with different surface morphologies, a smooth and rough surface area, were analyzed. The Mg composition ratio before annealing was 2.41, while the Mg composition ratio decreased significantly after annealing from 2.41 to 2.05 and 1.74 for the films with a smooth and rough surface area, respectively. Similarly, the Sn composition ratio decreased after annealing. We consider the mechanism of desorption of the constituent elements from the surface of the Mg$_2$Si$_{1-x}$Sn$_x$ films. It should be noted that in this study metallic Mg and Sn chips were used as a sputtering-target material. The Mg-Sn system has a eutectic temperature of 203°C when the Sn molar ratio (Sn$_x$) is higher than 0.33 (Sn$_x$ > 0.33) [17]. Furthermore, the vapor pressure of Mg is 10$^{12}$ times higher than that of Sn at 400°C [18]. Thus, excess isolated Mg atoms in Mg-rich Mg$_2$Si$_{1-x}$Sn$_x$ films may result in eutectic reaction with isolated Sn atoms even at an annealing temperature of 400°C. The dominant desorption of Mg atoms as compared to Sn atoms may also occur during annealing at 400°C.

The chemical composition ratio of the Mg$_2$Si$_{1-x}$Sn$_x$ films formed on the (100) CaF$_2$ substrates was analyzed using EDS as a function of Mg/Mg$_2$Si (Sn). EDS analysis was performed on the smooth surface area. Figure 4 shows the obtained composition ratio, x and y of the smooth surface for the
Mg$_{2y}$Si$_{1-x}$Sn$_x$ films after annealing at 400°C as a function of the Mg/Mg$_2$Si (Sn) value. The inset in Fig 4 shows a picture of the surface of the Mg$_{2.05}$Si$_{0.69}$Sn$_{0.31}$ films with Mg/Mg$_2$Si (Sn) = 0.012. As the number of Mg chip increases, the Mg composition ratio of the smooth surface area increases from 1.37 to 3.43, and it almost becomes stoichiometric Mg composition of 2.05 at smooth surface area for the Mg$_{2y}$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012, while the Sn composition ratio of the smooth surface area was almost constant at 0.31. The obtained composition of Mg$_{2.05}$Si$_{0.69}$Sn$_{0.31}$ at Mg/Mg$_2$Si (Sn) = 0.012 agrees well with the x value of 0.31, which was predicted from the Vegard’s law, as previously mentioned. The Mg composition of the rough surface area for Mg$_{2y}$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012 was much smaller than 2, as shown in Table I. Similarly, the Mg composition of the rough surface area for the Mg$_{2.05}$Si$_{0.69}$Sn$_{0.31}$ films with Mg/Mg$_2$Si (Sn) = 0.032 was smaller than 2, although the Mg composition of the smooth surface area for Mg$_{2y}$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.032 is 3.43 as shown in Fig. 4. This indicates the formation of Mg vacancy (V$_{Mg}$) at the rough surface area for Mg$_{2y}$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012 and 0.032. The Mg composition value at the rough surface area differs, and this difference was related to the measurement point. Consequently, the systematical evaluation of the Mg composition value of the rough surface area will be needed.

![Before annealing](image1.png) ![After annealing](image2.png)

**Fig. 2** Optical microscope images of the surface of Mg$_2$Si and Mg$_{2.05}$Si$_{0.69}$Sn$_{0.31}$ films before and after annealing.

![EDS mapping](image3.png)

**Fig. 3** EDS mapping images of Mg, Si and Sn measured on the rough surface area for Mg$_{2.05}$Si$_{0.69}$Sn$_{0.31}$ films after annealing at 400°C.

| Conditions                      | Mg (y) | Si (1-x) | Sn (x) |
|--------------------------------|--------|----------|--------|
| before annealing               | 2.41   | 0.57     | 0.43   |
| after annealing smooth surface area | 2.05   | 0.69     | 0.31   |
| after annealing rough surface area | 1.74   | 0.79     | 0.21   |

**Table I** Composition ratio of Mg$_{2y}$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012.
3.2 Electrical properties

Figure 5 shows the result of the Hall effect measurements for the Mg$_x$Si$_{1-x}$Sn$_x$ films deposited on the c-plane sapphire substrates and annealed at 400°C, as a function of Mg/Mg$_2$Si (Sn). Attention should be paid to the fact that the measured area includes both the rough and the smooth surface area. As mentioned above, the Mg$_x$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.031 and 0.062 only have a smooth surface area, while the Mg$_x$Si$_{1-x}$Sn$_x$ films with Mg/Mg$_2$Si (Sn) = 0.012 and 0.032 have a rough surface area about 50% and over 90% of the whole surface area, respectively. On the other hand, the chemical composition ratio, x and y for the Mg$_x$Si$_{1-x}$Sn$_x$ films in Fig. 4 was measured at the smooth surface area. In Fig. 5, all the samples after annealing at 400°C showed a p-type conductivity. The hole density and mobility showed a tendency to increase with increasing Mg/Mg$_2$Si (Sn). Usually, the hole density decreases as the excess Mg content increases in Mg$_2$Si due to an increase in interstitial Mg atoms, which act as a donor in Mg$_2$Si. However, the hole density of the Mg$_x$Si$_{1-x}$Sn$_x$ films increased as Mg/Mg$_2$Si (Sn) increases as shown in Fig. 5. There are two possible reasons for this. The first reason is the low eutectic temperature of 203°C in the higher Sn molar ratio (Sn$_x$) sample where Sn$_x$ was over 0.33 in the Mg-Sn system [17]. The other is the high vapor pressure of Mg, which is 10$^{12}$ times higher than that of Sn at 400°C [18]. Thus, excess isolated Mg atoms in the Mg-rich Mg$_x$Si$_{1-x}$Sn$_x$ films may result in eutectic reaction with isolated Sn atoms, and dominant vaporization of Mg atoms may occur when annealing at 400°C. These phenomena may be enhanced by increasing the Mg content in the Mg$_x$Si$_{1-x}$Sn$_x$ films which due to an increase in the number of Mg atoms surrounding the Sn atoms. To decrease in hole concentration, desorption of the Mg atoms during annealing should be suppressed: optimizations of deposition and annealing conditions are underway.
Fig. 5 Result of the Hall effect measurements for Mg$_7$Si$_{1-x}$Sn$_x$ films annealed at 400℃ as a function of Mg/Mg$_2$Si (Sn). The red closed circles and blue open squares represent the hole density and hole mobility, respectively.

3.3 Result of the first-principles calculation

First-principles calculation was performed to clarify the origin of p-type conductivity for the Mg$_7$Si$_{1-x}$Sn$_x$ films. Two types of Sn-related point defect in the silicide lattice were considered: for Sn substitution at Si site (Sn$_{Si}$) and for Sn substitution at Si site with Mg vacancy (Sn$_{Si}$+V$_{Mg}$). Figure 6 shows the DOS profiles of Sn$_{Si}$ (Mg$_7$Si$_{0.9}$Sn$_{0.1}$ = Mg$_7$Si$_{0.7}$Sn$_{0.3}$ and Sn$_{Si}$ + V$_{Mg}$ (Mg$_{0.9}$Si$_{10}$Sn$_{0.1}$ = Mg$_{1.8}$Si$_{0.7}$Sn$_{0.3}$). Sn$_{Si}$ (Mg$_{5}$Si$_{10}$Sn$_{0.1}$Sn$_{6}$) shows the intrinsic property, while Sn$_{Si}$ + V$_{Mg}$ (Mg$_{0.9}$Si$_{10}$Sn$_{0.1}$Sn$_{6}$) shows a p-type conductivity, judging from the positions of their fermi-levels (E$_F$). From the total energy obtained by first-principles calculation, we calculated the formation energy of the point defects in the Mg$_7$Si$_{1-x}$Sn$_x$ crystals. The formation energy (ΔE) of Sn$_{Si}$ and Sn$_{Si}$+V$_{Mg}$ can be calculated using Eqs. (1) and (2), respectively. Here, E(material) denotes the total energy of the single crystalline material. Table II shows the type of conductivity and the formation energy of the Mg$_7$Si$_{1-x}$Sn$_x$ crystals that contain a few types of point defects, which were obtained by first-principles calculation.

\[
\Delta E (Sn_{Si}) = E(Mg_{5.4}Si_{27-x}Sn_x) + xE(Si) - E(Mg_{5.4}Si_{27}) - xE(Sn) \quad (1)
\]

\[
\Delta E (Sn_{Si} + V_{Mg}) = E(Mg_{5.4}Si_{27-x}Sn_x) + xE(Si) + yE(Mg) - E(Mg_{5.4}Si_{27}) - xE(Sn) \quad (2)
\]

There were no significant influences of the lattice points occupied by two types of defects, Sn$_{Si}$ and V$_{Mg}$, on the DOS profiles and the total energies. The formation energy of Sn$_{Si}$+V$_{Mg}$ (Mg$_{0.9}$Si$_{10}$Sn$_{0.1}$) (0.342 eV/cell) is smaller than that of V$_{Mg}$ (Mg$_{0.9}$Si$_{27}$) (0.343 eV/cell) and Sn$_{Si}$ (Mg$_{5}$Si$_{18}$Sn$_9$) (0.470 eV/cell), which indicates that Mg$_{0.9}$Si$_{18}$Sn$_9$ could be easily formed when compared with the Mg vacancy in Mg$_7$Si and pure ternary Mg$_{5}$Si$_{18}$Sn$_9$. Thus, we believe that the origin of the p-type conductivity for Mg$_7$Si$_{1-x}$Sn$_x$ films could be due to a combination of two types of defects: Sn substitution at Si site (Sn$_{Si}$) and Mg vacancy (V$_{Mg}$).
Thus, we believe that the origin of the p-type conductivity could be easily formed when compared with Mg vacancy in MgSi and pure ternary Mg$_{54}$Si$_{18}$Sn$_9$. Thus, we believe that the origin of the p-type conductivity could be due to a combination of two types of defects: Sn substitution at Si site (Sn$_{Si}$) and Mg vacancy (V$_{Mg}$).
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