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Improvement of Power Factor in the Room Temperature Range of $Mg_2Sn_{1-x}Ge_x$

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Abstract

In this work, we investigated the effect of incorporating Ge into Mg_2Sn thin film, deposited on Al_2O_3(0001) (sapphire c-plane) substrate using molecular beam epitaxy (MBE), as well as the influence of the Mg/Sn supply ratio. We demonstrated that a low ratio of Sn to Mg improved the thin film's quality, while the incorporation of Ge atoms into the Sn sites resulted in superior thermoelectrical properties. The optimal power factor value obtained was $S^2\sigma$ = 0.2 mW m^{-1} K^{-1} at 300K.

1. Introduction

Thermoelectric (TE) thin films are a promising environment-friendly solution for power energy generation due to their capability to convert waste heat into electricity, or vice versa, based on the Seebeck, Peltier, and Thomson effects. In addition, they are lightweight and can be synthesized on different kinds of substrates, which offers the possibility of developing novel bendable and compact TE devices [1,2]. In the past years, Magnesium-based compounds (Mg_2X, X= Si, Ge and Sn) have been studied as a potential low-cost thermoelectric material. Although a significant progress has been made to optimize the *ZT* (figure of merit) of the bulk materials, the studies on Mg-based thin films are still limited.

The preferential growing method is RF magnetron sputtering, as a result, polycrystalline films are obtained with a (111) axial-preferred orientation perpendicular to the surface. In the case of polycrystalline samples, the correlation between parameters of control (substrate temperature, doping type and amount, annealing conditions, composition rate, among others) and thermoelectric properties can be difficult to determine due to effects of grain boundaries and intrinsic point defects [3]. However, in the case of epitaxial films, these correlations could be studied more easily.

In this work, we investigated the influence of the Mg/Sn ratio, and the incorporation of Ge doping on the thermoelectric properties of epitaxial Mg_2Sn thin films. We used molecular beam epitaxy (MBE) to deposit the thin films on sapphire substrates.

2. Methods and procedures

The $Mg_2Sn_{1-x}Ge_x$ ($0 < x < 0.25$) films were grown on sapphire (0001) substrates (Shinkosha) using an MBE system (Eiko, EV-500) under vacuum conditions of 10^{-6} – 10^{-7} Pa, see Table I [4]. Elemental magnesium (99.95 %), tin (99.999 %) and germanium (99.999 %) metals were evaporated using conventional Knudsen cells at 370-400°C for Mg, 1120-1180°C for Sn and 1050-1150°C for Ge. The relation between evaporation rate and cells temperature was determined by using a retractable quartz crystal microbalance (QCM) thicknesses monitor (Q-pod, Inficon), located the at substrate position. Based on our previous study, we fixed the substrate temperature at 400°C [4]. After 30-minutes depositions, films of 200-400 nm thickness were obtained. Afterward, the crystal structure was analyzed by ex-situ X-ray diffraction (XRD) using a powder diffractometer (Rigaku SmartLab 3). The film thicknesses were measured using a Dektak 6M surface profiler system. The thermoelectric properties were measured by the four-probe method from 300 K up to 525 K using a ZEM 3 (ULVAK Advance-Riko) apparatus under a He atmosphere. The Van der Pauw's electrical resistivity and Hall coefficient were measured using a Hall-effect measurement system (ResiTest 300).

Table I - List of samples $Mg_2Sn_{1-x}Ge_x$ experimentally tested for this study along with their synthesis conditions

Sample #	Nominal Composition	Mg rate (s^{-1} nm^{-2})	Sn rate (s^{-1} nm^{-2})	Ge rate (s^{-1} nm^{-2})
H1	Mg_2Sn + Sn	11.55	3.77	-
H2	Mg_2Sn	11.55	2.85	-
H3	Mg_2Sn	11.55	2.09	-
H4	Mg_2Sn	11.55	1.57	-
G1	$Mg_2Sn_{0.88}Ge_{0.12}$	11.55	1.36	0.19
G2	$Mg_2Sn_{0.85}Ge_{0.15}$	11.55	1.27	0.23
G3	$Mg_2Sn_{0.82}Ge_{0.18}$	11.55	1.20	0.26
G4	$Mg_2Sn_{0.88}Ge_{0.12}$	12.00	1.36	0.19

3. Results and Discussion

Figure 1 shows the XRD patterns of the Mg_2Sn films deposited by varying the rate of Sn evaporation (H1-H4) and Ge

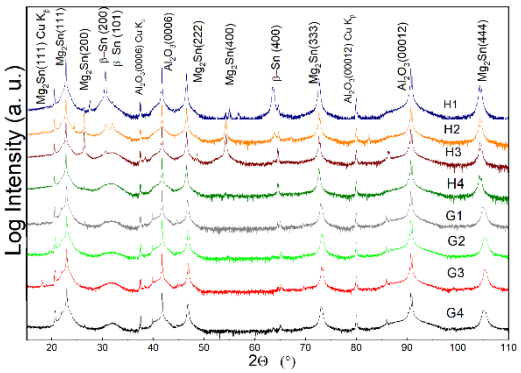

Fig. 1 The XRD pattern of the $Mg_2Sn_{1-x}Ge_x$ films deposited on sapphire substrates (111)

incorporation (G1-G4). The effect of the Mg/Sn ratio was investigated first, (H1-H4, Figure 1). The XRD patterns had strong epitaxial $Mg_2Sn(nnn)$ peaks (n = 1-4) and small residual β-Sn (200) and (220) peaks. As the Sn rate decreases, the β-Sn peaks also decrease. Probably, the Mg atoms arriving at the surface immediately react with Sn, or leave the surface, because the Mg vapor pressure is much higher than Sn. When the evaporation rate of Sn is below 2 atoms s^{-1} nm^{-2}, all Sn has reacted with Mg, leaving no residual Sn. In the case of the Ge series (G1-G4, Fig. 1), peak shifts at $Mg_2Sn(nnn)$ series were observed, suggesting a substitution of Ge in Sn site.

Figure 2 shows the dependence of Seebeck coefficient (S) with temperature. In the case of the Hs series (H1-H4), there is a transition from n-type (S_{H1} = -50 μV/K at 300 K) to p-type (S_{H4} = 50 μV/K at 300 K) with the Sn rate. This transition could be associated with the residual β-Sn phase. And additionally, a transition from a p- to an n-type with temperature (H2-H4 around 350-400 K) is observed, which may be resulted from the narrow band gap, about 0.3 eV, of Mg_2Sn. Regarding Ge series (G1-G4), Figure 2 shows a stronger p-type behavior (S = 270 μV/K at 300 K) and a stronger temperature dependence, suggesting defects formation. Liu et al. [3] reported the influence of intrinsic point defects on electronic transport properties of Mg_2X (X= Si, Ge, Sn) systems. They showed that Mg vacancies and interstitial Mg are assumed to be the main defects in Mg_2X compounds according to their relatively low formation energies. Mg vacancies (V_{Mg}) and interstitial Mg (I_{Mg}) behave as acceptor and donor sites, respectively.

The XRD data suggests that the growing surface is Mg-rich (Sn deficient) regime, but the formation of interstitial Mg is small than Mg vacancies because the low condensation rate of Mg [6]. Probably, the majority point defect in our films are Mg vacancies (V_{Mg}) at the 8c (1/4 1/4 1/4) site. This point defect is ionized and generate hole carriers in Mg_2Sn, according to the following equation: $V_{Mg} \rightarrow V_{Mg2-} + 2\ h+$ [3,5]. With addition of Ge, the atom diffusivity decreases, because of the small ionic radius and the high melting point of Ge. In

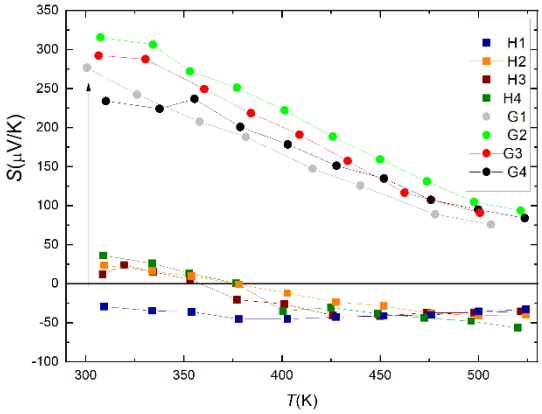

Fig. 2 Temperature dependence of Seebeck coefficient of $Mg_2Sn_{1-x}Ge_x$ films

case of the Sn, the ionic radius is close to that of Mg and Sn stays liquid at the growth temperature (400°C). On the other hand, the ionic radius of Ge is smaller than Mg, and it becomes solid. Accordingly, the Mg vacancies increase, making the acceptor level slightly above the top of the semiconductor's valence.

Figure 3 shows plots of conductivity (σ) versus temperature (T). All the films show a semiconductor behavior with temperature. As the Sn to Mg ratio decrease, the conductivity rises, consistent with the decreasing of the residual β-Sn phase. In the case of the Ge-added samples, the conductivity systematically decreases with the amount of Ge, suggesting an increasing in the number of defects which affect the conductivity.

As we expected, the power factor ($S^2\sigma$) values for these undoped Mg_2Sn compositions were not very high: S_{H4} = 0.04 mW m^{-1} K^{-1} at 300 K, however, in the case of Ge series it was around S_{G2} = 0.2 mW m^{-1} K^{-1} at 300 K.

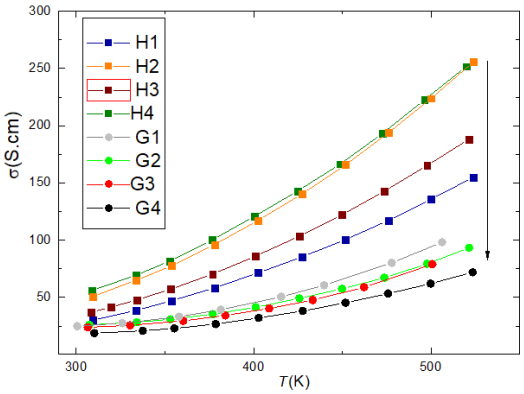

Fig.3 Temperature dependence of electrical conductivity of the $Mg_2Sn_{1-x}Ge_x$ films

4.Conclusions

Thin films of $Mg_2Sn_{1-x}Ge_x$ were fabricated on sapphire c-plane substrates using MBE. We demonstrated the growth of high-quality crystalline epitaxial films of $Mg_2Sn_{1-x}Ge_x$ thermoelectric compounds by structural characterization and electrical transport measurements. The incorporation of Ge suggests an increase of defects, along with improved p-type behavior and reduced conductivity. The optimal power factor value was $S^2\sigma$ = 0.2 mW m^{-1} K^{-1} at 300 K.

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References

[1] I. Petsagkourakis, Sci. Technol. Adv. Mater. **19**, 836 (2018).
[2] T. Mori and S. Priya, MRS Bull. **43**, 176 (2018).
[3] X. Liu *et al.*, Adv. Electronic Mater. **2**, 1500284 (2016).
[4] T. Aizawa *et al.*, J. Vac. Sci. Technol. A**37**, 061513 (2019).
[5] W. Saito *et al.*, Scientific reports **10**, 2020 (2020)
[6] J. E. Mahan, *et al*., Phys. Rev. B 54, 16965 (1996).