Thermoelectric Properties of Amorphous Zr-Ni-Sn Thin Films Deposited by Magnetron Sputtering

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n-Type Zr-Ni-Sn thermoelectric thin films with thickness of 60 nm to 400 nm were deposited by radiofrequency magnetron sputtering. The microstructure of the Zr-Ni-Sn thin films was examined by x-ray diffractometry and high-resolution transmission electron microscopy, revealing an amorphous microstructure. The thermal conductivity of the amorphous films was measured by the ultrafast laser pump-probe thermoreflectance technique, revealing values of $1.4 \text{ W m}^{-1} \text{ K}^{-1}$ to $2.2 \text{ W m}^{-1} \text{ K}^{-1}$, smaller than that of bulk material because of the amorphous microstructure of the films. The effects of the sputtering power on the composition, Seebeck coefficient, and electrical conductivity of the films were investigated. The largest Seebeck coefficient and power factor were achieved at 393 K, being $-112.0 \mu\text{V K}^{-1}$ and $2.66 \text{ mW K}^{-2} \text{ m}^{-1}$, respectively. The low thermal conductivity and high power factor indicate that amorphous Zr-Ni-Sn thin films could be a promising material for use in thermoelectric microdevices.

Key words: Zr-Ni-Sn, thin films, amorphous structure, magnetron sputtering, thermoelectric properties

INTRODUCTION

Thermoelectric materials and devices have attracted considerable interest due to their wide applications in energy harvesting, interstellar spacecraft, chip cooling, and wireless sensing.^{1,2} The dimensionless thermoelectric figure of merit ZT of a material is defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity, including the carrier thermal conductivity κ_c and the lattice thermal conductivity κ_l . $S^2\sigma$ is defined as the power factor. Recently, bulk ternary half-Heusler (HH) compounds such as MNiSn and MCoSb ($M = \text{Ti, Zr, and Hf}$) have exhibited excellent transport properties and ZT values close

to those of state-of-the-art materials such as PbTe and Bi_2Te_3 -based compounds.^{3–8} For MNiSn-based HH compounds, it has been found that a small amount of Sb doping can enhance ZT , with reliable values of 0.8 to 1.0.^{9,10} For MCoSb-based HH compounds, ZT values have been improved to 0.51 owing to a remarkable reduction of the thermal conductivity.^{11,12}

Besides bulk HH compounds, HH thin films have also been investigated because thin films have potential applications in portable devices, power electronics, wireless sensor networks, and other fields.^{13–16} There is an urgent need to develop thin-film materials with high ZT values. High-quality NiMnSb and NiYBi thin films have been deposited by radiofrequency (RF) magnetron sputtering or molecular-beam epitaxy.^{17–19} MNiSn-based HH thin films have also been synthesized by magnetron sputtering or electron beam deposition, exhibiting a largest Seebeck coefficient and power factor on the

order of tens of $\mu\text{V K}^{-1}$ and on the order of $0.1 \text{ mW K}^{-2} \text{ m}^{-1}$, respectively.^{20–22}

The reliable ZT values of crystalline HH materials have been limited to around 1.0 so far, mainly due to the high thermal conductivity of HH compounds.²³ Provided that the microstructure of a thermoelectric material is amorphous, the lattice thermal conductivity κ_l of the material can be minimized and the total thermal conductivity κ can be greatly reduced, which hence should enhance the ZT value. For various kinds of thermoelectric materials such as Zn_4Sb_3 , Cu-Ge-Te, Ge, and Si, amorphous microstructure has indeed resulted in good thermoelectric properties.^{24–26} Nolas et al. suggested that amorphous HH alloys could be high-efficiency thermoelectric materials.²⁷

However, the thermoelectric properties of amorphous HH alloys have not been reported in the literature as far as we know. In this work, we synthesized n -type Zr-Ni-Sn thin films with an amorphous microstructure by RF magnetron sputtering and characterized the transport properties of the as-deposited films.

EXPERIMENTAL PROCEDURES

n -Type Zr-Ni-Sn films were deposited on SiO_2 (300 nm thick)/Si substrates at room temperature (RT) by RF magnetron sputtering. A hot-pressed $\text{Zr}_{34}\text{Ni}_{31}\text{Sn}_{35}$ target (diameter, 3 inches; 99.95 at.%) was used. The base pressure in the sputtering chamber was below 1.5×10^{-4} Pa, the deposition pressure was 0.8 Pa, and the Ar gas flow was 10 sccm. The sputtering power was 80 W, 100 W, 120 W or 140 W. Samples of three sizes (4 mm $\times$ 16 mm, 10 mm $\times$ 10 mm, and 4 mm $\times$ 4 mm) were simultaneously deposited. The 4 mm $\times$ 16 mm samples were used for Seebeck measurements, whereas the 10 mm $\times$ 10 mm and 4 mm $\times$ 4 mm samples were used for Hall testing and other measurements. The film thickness was 60 nm to 400 nm for 1 h of sputtering.

The microstructure of the thin films was characterized by transmission electron microscopy (TEM, model JEM-2011, Japan Electron Optics Laboratory Co., LTD, Japan) and x-ray diffractometry (XRD) with a D/max-RB diffractometer (Rigaku, Japan) using Cu K_α radiation. The film composition was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, VISTA-MPX, Varian Inc., USA). σ was measured using the van der Pauw method on a four-probe station with a temperature-controlled stage. S was measured by a customized setup with a good accuracy.²⁸ The carrier concentration n was measured using a Hall measurement setup (Resis-Hall test DC-8340, TOYO, Japan) with Ar gas protection. The mobility μ was obtained from the equation $\mu = \sigma/ne$, where e is the charge of an electron. The κ of the films at RT was measured by the ultrafast laser pump-probe

thermoreflectance technique, whose details were mentioned in Refs. 29,30.

RESULTS AND DISCUSSION

The composition of the Zr-Ni-Sn films deposited with different sputtering powers is summarized in Table I, and the dependence of the concentration of each element on the sputtering power is plotted in Fig. 1. The concentration of Ni gradually decreased, that of Zr increased, and that of Sn was stable as the sputtering power was raised from 80 W to 140 W. To study the microstructure of the films, XRD and high-resolution TEM (HRTEM) were carried out. Figure 2a shows the diffraction patterns of the as-deposited Zr-Ni-Sn films. No sharp peak was found, except for the diffraction peaks from the Si substrate. A broadened bump feature was observed, indicating an amorphous microstructure. Figure 2b shows an HRTEM image of the sample deposited at sputtering power of 80 W, which exhibited the best thermoelectric properties as shown in Table I. The HRTEM image clearly shows that the Zr-Ni-Sn film is not crystallized. The selected-area electron diffraction (SAED) image in Fig. 2b presents two fuzzy rings that cannot be identified as Zr-Ni-Sn alloy or other binary alloys. Therefore, it can be concluded that the sputtered Zr-Ni-Sn thin film is amorphous, which may lead to low thermal conductivity.²⁴

Figure 3a shows the Seebeck coefficients of the Zr-Ni-Sn thin films deposited with different powers as a function of temperature. The maximum error of the Seebeck coefficient measurement is within $\pm 8.4\%$ according to our previous work.²⁸ For the samples deposited at 80 W and 100 W, the curves of S show a concave-upward trend, whereas the variation of S for the samples deposited at 120 W and 140 W exhibits a concave-downward trend. At RT, the sample deposited at 140 W has the largest S value of $-83.5 \mu\text{V K}^{-1}$ among the four samples. The maximum S over the whole temperature range occurs at 393 K for the sample deposited at 80 W, being $-112.0 \mu\text{V K}^{-1}$. For HH alloys, S , n , and μ may be calculated by the following equations:^{31,32}

$$|S| = \left| \frac{k_B}{e} \left[\eta - \left(r + \frac{5}{2} \right) \right] \right|, \quad (1)$$

$$n = 2 \left(\frac{2\pi m^* k_B T}{h^2} \right)^{3/2} \exp(\eta), \quad (2)$$

$$\mu = \frac{4}{3\pi^{1/2}} \left(r + \frac{5}{2} \right) \frac{e\tau_0 (k_B T)^r}{m^*}, \quad (3)$$

$$\eta = (E_F - E_C)/(k_B T), \quad (4)$$

Table I. Composition and transport properties (393 K) of Zr-Ni-Sn films deposited with different powers

Sputtering Power (W)	Zr/Ni/Sn Atomic Ratio	n (10^{21} cm^{-3})	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	σ (10^3 S cm^{-1})	S ($\mu\text{V K}^{-1}$)	$S^2\sigma$ ($\text{mW K}^{-2} \text{ m}^{-1}$)
80	27.0/40.4/32.6	0.27	49.1	2.12	-112.0	2.66
100	27.7/39.1/33.2	10.9	1.65	2.88	-33.73	0.33
120	29.5/38.2/32.3	2.91	7.33	3.41	-42.10	0.60
140	29.6/37.5/32.8	1.02	20.4	3.33	-31.17	0.32

Fig. 1. Composition of Zr-Ni-Sn films as a function of sputtering power.

$$\Gamma(m+1) = m\Gamma(m), \quad (5)$$

where h is Planck's constant, m^* is the effective mass of the electron, e is the electron charge, T is the temperature, k_B is Boltzmann's constant, η is the reduced chemical potential, r is the scattering factor, and E_F and E_C are the Fermi energy and the energy of the conduction-band bottom. Therefore, S is related with n , μ , and r according to Eqs. 1–3. The composition of the Zr-Ni-Sn films changed as the sputtering power was varied, and thus all the n , μ , and r values may be different for these films. Generally, the absolute value of S of HH alloys decreases as n increases,³² which is also valid for the Zr-Ni-Sn films deposited at 80 W, 100 W, and 120 W. However, the sample deposited at 140 W showed the second smallest n and smallest absolute value of S . This contradiction is possibly due to the variation of the scattering factor r . Maybe the scattering mechanism is different for the film deposited at 140 W, because this particular sample has the maximum Zr content and minimum Ni content. More work on analysis of the carrier concentration and scattering mechanism in Zr-Ni-Sn films needs to be done in the future. Some S data for HH alloys with similar carrier concentration from the literature are also summarized in Fig. 3a. The S values of the samples in Refs. 32,33 (with n of $0.23 \times 10^{21} \text{ cm}^{-3}$ to $0.53 \times 10^{21} \text{ cm}^{-3}$) are close to that of the film deposited at 80 W. The S value of the

Fig. 2. (a) XRD patterns of Zr-Ni-Sn films sputtered with different powers, and (b) HRTEM and SAED images of Zr-Ni-Sn film prepared with sputtering power of 80 W.

sample with $n \approx 15 \times 10^{21} \text{ cm}^{-3}$ in Ref. 33 is close to that of the film deposited at 100 W.

Figure 3b summarizes the temperature dependence of the electrical conductivity of the films. The error of the σ measurement is estimated to be less

Fig. 3. (a) Seebeck coefficient and (b) electrical conductivity of Zr-Ni-Sn films deposited with different sputtering powers as a function of temperature.

than $\pm 3.0\%$, taking into account the errors due to the geometry and the nonuniformity of samples as well as the error of the instrument (Agilent 34970A data acquisition unit) in the van der Pauw method.³⁴ The σ value of the Zr-Ni-Sn films does not vary significantly with temperature for each sample. In general, σ increases with increase of the sputtering power, and the sample deposited at 80 W has the smallest σ . The electrical conductivity of our Zr-Ni-Sn films is larger than those of other M-Ni-Sn thin films.^{21,22} Again, the σ value of the $\text{Hf}_{0.65}\text{Zr}_{0.35}\text{NiSn}_{0.98}\text{Sb}_{0.02}$ sample in Ref. 32 is similar to that of the Zr-Ni-Sn film deposited at 80 W. Taking into account both σ and S , our Zr-Ni-Sn film deposited at 80 W has similar thermoelectric properties compared with the $\text{Hf}_{0.65}\text{Zr}_{0.35}\text{NiSn}_{0.98}\text{Sb}_{0.02}$ sample in Ref. 32. Although the σ of the sample prepared at 80 W is the smallest among the four samples, its power factor $S^2\sigma$ becomes the largest when the temperature reaches 393 K owing to its maximum S , as shown in Fig. 4a. The largest value of $S^2\sigma$ is $2.66 \text{ mW K}^{-2} \text{ m}^{-1}$ at 393 K, which is larger than those of other M-Ni-Sn films because both S and σ of this sample are enhanced.^{21,22} In addition, for the samples deposited at 120 W and 140 W, the power

Fig. 4. Power factor of Zr-Ni-Sn films deposited with different sputtering powers as a function of temperature.

factors decrease with increasing T due to the reduction of S .

The time-domain ultrafast laser pump-probe thermoreflectance technique was used to measure the thermal conductivity of the amorphous Zr-Ni-Sn thin films at RT.^{29,30} In this method, the measured ratio of the in-phase to the out-of-phase signal ($-V_{\text{in}}/V_{\text{out}}$) as a function of the time interval (τ) between the pump beam and probe beam is fitted using a multilayered heat transfer model to obtain κ .^{29,30} Figure 5 shows the time-domain thermal reflectance signals of the samples deposited at 80 W, 100 W, 120 W, and 140 W, whose κ values were measured to be $1.40 \text{ W m}^{-1} \text{ K}^{-1}$, $1.35 \text{ W m}^{-1} \text{ K}^{-1}$, $2.20 \text{ W m}^{-1} \text{ K}^{-1}$, and $1.60 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The typical errors of the signals due to the uncertainties in the film thickness and the laser spot size are within $\pm 20\%$.³⁰ Although only the κ at RT was obtained due to the limitations of the equipment, these data provide useful information for Zr-Ni-Sn films since there is very little literature reporting the thermal conductivity of HH films. Table II lists typical values of thermal conductivity for M-Ni-Sn-based bulk materials and films. The thermal conductivity of Zr-Ni-Sn thin films was $1 \text{ W m}^{-1} \text{ K}^{-1}$ to $3 \text{ W m}^{-1} \text{ K}^{-1}$,³⁵ whereas that of Zr-Ni-Sn bulk alloys was about $6 \text{ W m}^{-1} \text{ K}^{-1}$ to $17 \text{ W m}^{-1} \text{ K}^{-1}$,^{11,32,33,36–38} which demonstrates that Zr-Ni-Sn films have lower thermal conductivity than their bulk counterparts. In addition, we prepared a bulk $\text{Zr}_{30}\text{Ni}_{40}\text{Sn}_{30}$ sample by hot-pressing Zn, Ni, and Sn powders (using the same method as applied to make the sputtering target), measured its thermal diffusivity using the laser flash method (TC-9000, Ulvac-Riko, Japan), and calculated its RT thermal conductivity as $\kappa = \lambda C_p \rho$, where λ is the measured thermal diffusivity ($2.658 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), C_p is the theoretical heat capacity ($0.302 \text{ J g}^{-1} \text{ K}^{-1}$), and ρ is the measured density (5.97 g cm^{-3}). The κ of bulk $\text{Zr}_{30}\text{Ni}_{40}\text{Sn}_{30}$ is

Table II. Summary of thermal conductivity of M-Ni-Sn-based bulk materials and films at RT

Material	κ at RT ($\text{W m}^{-1} \text{K}^{-1}$)	Type	Reference
Zr-Ni-Sn	1.4–2.2	Film	This work
TiNiSn	2.8	Film	35
Zr _{0.5} Hf _{0.5} NiSn	1.1	Film	35
Zr ₃₀ Ni ₄₀ Sn ₃₀	4.79	Bulk	This work
ZrNiSn	11.4	Bulk	36
ZrNiSn	5.9–17.2	Bulk	37
Zr _{0.25} Hf _{0.75} NiSn	5.37	Bulk	33
Hf _{0.65} Zr _{0.35} Ni _{1-x} Pt _x Sn _{0.98} Sb _{0.02}	4–7.5	Bulk	32
Zr _{0.5} Hf _{0.5} Ni _{0.5} Pd _{0.5} Sn _{0.99} Sb _{0.01}	3.1	Bulk	36
(Zr _{0.5} Hf _{0.5}) _{0.99} Ta _{0.01} NiSn	5.4	Bulk	38
Ti _{0.5} Zr _{0.25} Hf _{0.25} Co _{1-x} Ni _x Sb	3.35–4.50	Bulk	11

Fig. 5. Time-domain thermal reflectance signals of samples deposited at 80 W, 100 W, 120 W, and 140 W. The solid lines are fit curves to the measured data.

$4.79 \text{ W m}^{-1} \text{K}^{-1}$, which confirms that the κ of Zr-Ni-Sn material is closely related to the composition and synthesis method. Our thermal conductivity data obtained by the thermoreflectance technique are on the same order as other data reported for thin films, indicating that our measurement is reliable. From Table II, it can be seen that heavy elements such as Hf, Ta, Pt, and Sb may be added into M-Ni-Sn alloys to increase the disorder in the material and to reduce the thermal conductivity. Since the Zr-Ni-Sn films have an amorphous structure, the disorder in the alloy is prominent and hence the thermal conductivity is low. The resulting amorphous structure is similar to that achieved by adding heavy elements.

CONCLUSIONS

Amorphous *n*-type Zr-Ni-Sn thin film was synthesized by RF magnetron sputtering. The thermal conductivity of the film was measured to be $1.4 \text{ W m}^{-1} \text{K}^{-1}$ to $2.2 \text{ W m}^{-1} \text{K}^{-1}$ by the ultrafast laser pump-probe thermoreflectance technique, which was attributed to the amorphous microstructure. A Seebeck coefficient of $-112.0 \mu\text{V K}^{-1}$ and a power factor of $2.66 \text{ mW K}^{-2} \text{m}^{-1}$ were

achieved at 393 K for the film deposited at sputtering power of 80 W. The experimental data demonstrate that amorphous Zr-Ni-Sn thin film could be a promising material for use in thermoelectric microdevices because of its low thermal conductivity and high power factor.

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