

Preparation of n-type nano-scale MnSi_{1.7} films by addition of iron

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ABSTRACT

Nano-scale higher manganese silicide (MnSi_{1.7}) film with thickness of about 27 nm is prepared by thermal annealing of a bi-layer Si/MnSi_x ($x < 1.7$) at 650 °C. When the thermal annealing time is 25 min, the film is p-type from 300 K to 633 K. By increasing the thermal annealing time to 65 min, the film is still p-type around room temperature but transforms to n-type at high temperatures. The thermoelectric powers at 300 K and 633 K are +116 $\mu\text{V K}^{-1}$ and -321 $\mu\text{V K}^{-1}$, respectively. With addition of enough iron to the film, n-type MnSi_{1.7} film with lower electrical resistivity is obtained. The thermoelectric power reaches to -568 $\mu\text{V K}^{-1}$ at 533 K. As a result, the thermoelectric power factor of the nano-scale n-type MnSi_{1.7} film at 533 K is $3.6 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$. This value is greater than that of p-type bulk MnSi_{1.7} materials.

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1. Introduction

Thermoelectric semiconductors can be used directly to convert heat to electrical power or pump heat from cold surface to hot side, both without any moving parts or bulk fluids. However, they have not enjoyed widespread use because of its low thermoelectric efficiency [1]. The thermoelectric efficiency depends on the thermoelectric figure of merit, Z , of the semiconductor. This quantity is a combination of the thermoelectric power or Seebeck coefficient S , the electrical resistivity R , and the thermal conductivity K of the semiconductor:

$$Z = \frac{S^2}{RK} = \frac{P}{K} \quad (1)$$

where $P = S^2/R$ is called the thermoelectric power factor. When the thermal conductivity of the film is difficult to measure, the term P is usually used to characterize the thermoelectric properties. One approach to increasing Z is to search for semiconductors exhibiting an enhanced thermoelectric power.

Recent theoretical works have predicted that low dimensional semiconductors will result in the enhancement of Z , due to the quantum-mechanical nature of the motion of electrons through semiconductors [2–5]. The main mechanism for the enhancement is due to an increase of the density of states near the Fermi level. As a result, a sufficient density of charge carriers can exist in the semiconductor to maintain the electrical resistivity, but the Fermi energy is small, and this leads to a large S . Experimental observation of the enhancement of S has already been reported in Si/Ge super-

lattice thin films and Bi nano-wires. The thermoelectric power reaches to 50 mV K^{-1} or even higher [6,7]. An enhancement of ZT to a value of about 2.4 for super-lattices of Bi₂Te₃/Sb₂Te₃ and PbSeTe/PbTe at room temperature ($T \approx 300 \text{ K}$) was also reported [8–11].

It is well known, however, that Ge is expensive and the materials for fabrication of the above super-lattices are toxic. Thus it is very interesting for us to look for other thermoelectric semiconductors which are cheap and non-toxic. MnSi_{1.7} materials are good candidates for thermoelectric applications. The source materials Mn and Si are cheap and non-toxic. In the past, the thermoelectric properties of MnSi_{1.7} bulk materials and thin films were investigated [12–27]. The thickness of the films ranges from 50 nm to 20 μm . Both the bulk materials and the films are usually p-type. To our knowledge, the best value of thermoelectric power factor at 873 K for p-type bulk MnSi_{1.7} materials is $2.4 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ [14]. Recently, n-type MnSi_{1.7} films with a thickness of about 112 nm were prepared by magnetron sputtering [22,24,26,28]. The reason for n-type conductivity was suspected of iron impurity which was added unintentionally during the preparation of the films. The best value of thermoelectric power factor at 683 K for the n-type MnSi_{1.7} films was about $1.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ [26,28]. In this paper, n-type nano-scale MnSi_{1.7} films are prepared on thermally oxidized silicon substrates by addition of iron. The thermoelectric power factor of the nano-scale n-type MnSi_{1.7} film at 533 K reaches to $3.6 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$. This value is greater than that of p-type bulk MnSi_{1.7} materials.

2. Experimental

The nano-scale MnSi_{1.7} and β -FeSi₂ films shown in Table 1 were prepared by solid phase reaction in an electron beam evaporation system. The schematic diagram of the electron beam evaporation system can be found elsewhere [25,27].

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Table 1
Parameters of the nano-scale $\text{MnSi}_{1.7}$ films s1–4 and $\beta\text{-FeSi}_2$ film s5. Samples s1 and s2 are un-doped while s3 and s4 are Fe-doped. The $\text{MnSi}_{1.7}$ film thickness is about 27 nm.

Sample	Carrier type	Annealing time (min)	Seebeck coeff. at 300 K ($\mu\text{V K}^{-1}$)	Seebeck coeff. at 633 K ($\mu\text{V K}^{-1}$)	Energy band gap (eV)
S1	p	25	+122	+91	–
S2	p \rightarrow n	65	+116	–321	0.92 ^a
S3	p \rightarrow n	60	+237	–276	0.63 ^a
S4	n	60	–191	–344	0.64 ^b
S5	n	60	–	–274	0.82 ^b

^a Calculated from Eq. (8).

^b Calculated from Eq. (5).

The base pressure of the system was 5×10^{-4} Pa. The substrates were thermally oxidized silicon wafers. The silicon dioxide (SiO_2) layer has a thickness of about 450 nm. Si, MnSi, and FeSi_2 source materials were contained in graphite crucibles. The purity of Si is 99.999 at.%. The purity of MnSi and FeSi_2 is 99.9 at.%. For samples s1 and s2, a bi-layer Si/MnSi_x was deposited on the substrate with the silicon layer on the top. For samples s3 and s4, a three-layer Si/MnSi_x/FeSi₂ was deposited on the substrate. Sample s5 with a bi-layer FeSi₂/Si was also prepared to investigate the possible influence of the FeSi₂ layer on the electrical property of MnSi_{1.7} film. These layers were deposited on substrates at about 120 °C. The Si layer thickness was about 40 nm. The deposition rate of silicon was about 40 nm min^{–1}. The silicon layer was used as the consuming material for the formation of MnSi_{1.7} phase. Due to the high vapor pressure of manganese, a thin MnSi_x ($x \approx 0.16$) layer was deposited from evaporation of the MnSi source material [29,30]. For sample s5, the $\beta\text{-FeSi}_2$ film thickness was about 23 nm. The thicknesses of FeSi₂ layers in samples s4 and s3 were about 10 nm and 5 nm, respectively. After deposition, the samples were thermally annealed in situ at about 450 °C for 20 min. The in situ thermal annealing caused the formation of manganese silicides, such as Mn₃Si₃ and/or MnSi [31,32]. Once the manganese silicides formed, it was very difficult to oxidize them [33,34]. Then the samples were taken out from the chamber and put them in another place of the chamber, where the temperature can be reached to 650 °C. Finally, the samples s2–5 were thermally annealed in the chamber (1.2×10^{-3} Pa) at about 650 °C for 60 min or 65 min for the complete formation of MnSi_{1.7} or $\beta\text{-FeSi}_2$ phase. For sample s1, the annealing time was 25 min.

During the electron beam evaporation process, the thickness of each layer was monitored in situ by an optical method. Three reference glass plates were placed near the substrate. For measuring the thickness of transparent silicon layer, interference of light occurred naturally between beams reflected from the film surface and film-substrate interface. The intensity of the reflected light underwent oscillations

as a function of the optical film thickness. The maximum values of light intensity occurred at film thickness t equal to:

$$t = \frac{m\lambda}{4n_0} \quad (m = 1, 3, 5, \dots) \quad (2)$$

where m is an odd integer, $\lambda = 546$ nm, and n_0 is the index of refraction for the silicon layer ($n_0 \sim 3.4$) [35,36]. For values of t halfway between these, the reflected intensity is minimum. For monitoring the thickness of the MnSi_x and FeSi₂ layers, the change of the transmitted light intensity before and after the layer deposition was used as a reference.

$$I_t = I_i \exp(-\alpha t) \quad (3)$$

where α is the absorption coefficient of the layer, I_i and I_t are the transmitted light intensity before and after the layer deposition, respectively. The thickness and composition of the MnSi_{1.7} and $\beta\text{-FeSi}_2$ films were estimated by Auger electron spectroscopy (AES) depth profiles obtained in a PHI-700 system. The thermoelectric power and electrical resistivity were measured by the two-probe method [20–28].

3. Results

Fig. 1 shows the AES depth profiles of Mn, Si, O, and Fe for un-doped MnSi_{1.7} film s2 (a), Fe-doped MnSi_{1.7} film s4 (b), and $\beta\text{-FeSi}_2$ film s5 (c), respectively. The open triangles, squares, circles, and solid points represent Si, Mn, O, and Fe, respectively. As shown in Fig. 1(a) for un-doped sample s2, the depth profiles exhibit that the level of manganese in the MnSi_{1.7} film is about 20 at.%. The MnSi_{1.7} film thickness is about 27 nm. For Fe-doped sample s4 shown in

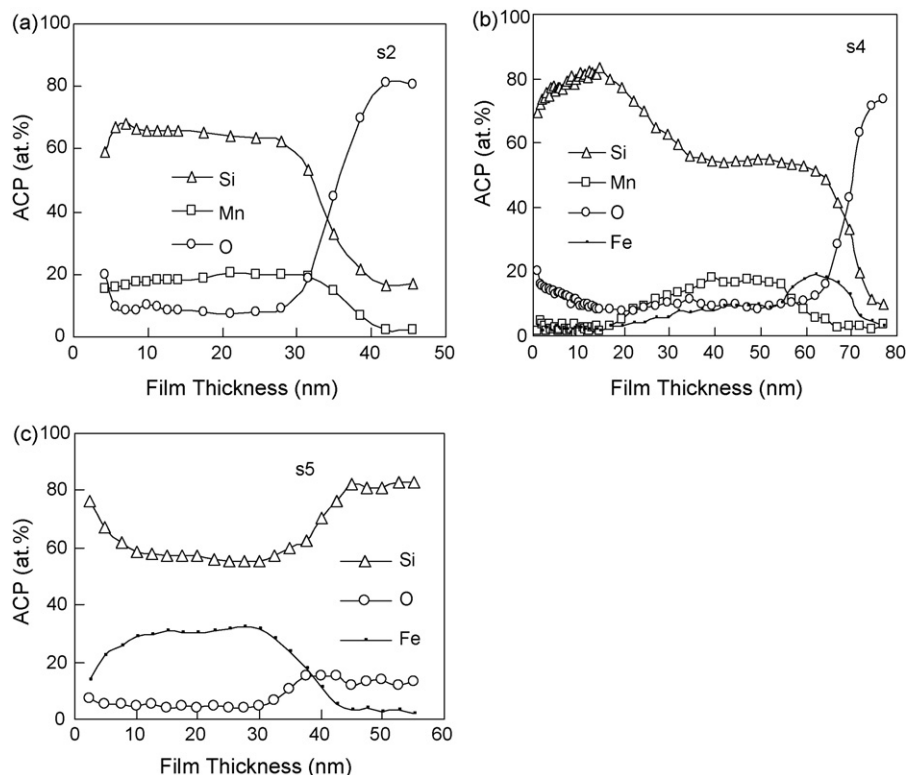


Fig. 1. AES depth profiles of Mn, Si, O, and Fe for un-doped MnSi_{1.7} film s2 (a), Fe-doped MnSi_{1.7} film s4 (b), and $\beta\text{-FeSi}_2$ film s5 (c). The MnSi_{1.7} film thickness is about 27 nm. The FeSi₂ layer thickness in sample s4 is about 10 nm. The $\beta\text{-FeSi}_2$ film thickness is about 23 nm.

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