Materials Chemistry and Physics 146 (2014) 346–353

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Layer-by-layer deposition of $MnSi_{1.7}$ film with high Seebeck coefficient and low electrical resistivity

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HIGHLIGHTS

- $MnSi_{1.7}$ films are deposited layer by layer by a short time interruption of film deposition.
- The thickness of each $MnSi_{1.7}$ layer can be controlled in the nano-scale.
- $MnSi_{1.7}$ films have a higher Seebeck coefficient and a lower electrical resistivity.
- The quantum size effect in n-type $MnSi_{1.7}$ films is rather strong.

ARTICLE INFO

Article history:
Received 28 September 2012
Received in revised form
24 May 2013
Accepted 19 March 2014

Keywords:
Semiconductors
Vacuum deposition
Auger electron spectroscopy (AES)
Thermoelectric effect

ABSTRACT

A good thermoelectric material should have a high Seebeck coefficient, a low electrical resistivity, and a low thermal conductivity. For conventional thermoelectric materials, however, increasing the Seebeck coefficient also leads to a simultaneous increase in the electrical resistivity. In this paper, a method of layer-by-layer deposition of $MnSi_{1.7}$ film with high Seebeck coefficient and low electrical resistivity is developed. After deposition of the first $MnSi_{1.7}$ sub-layer, the deposition process is interrupted for several minutes, and then continues for another $MnSi_{1.7}$ sub-layer. Therefore, the $MnSi_{1.7}$ film contains two sub-layers for one interruption, three sub-layers for two interruptions, and so on. It is found that the n-type $MnSi_{1.7}$ film with two sub-layers has a higher Seebeck coefficient, −0.451 mV K^{-1}, and a lower electrical resistivity, 19.4 mOhm-cm, at 483 K as compared to that of without deposition interruption, −0.152 mV K^{-1} and 44.3 mOhm-cm. The p-type $MnSi_{1.7}$ film with three sub-layers also has a higher Seebeck coefficient, 0.238 mV K^{-1}, and a lower electrical resistivity, 5.5 mOhm-cm, at 733 K in comparison with that of without deposition interruption, 0.212 mV K^{-1} and 10.4 mOhm-cm.

1. Introduction

Thermoelectric materials can be used to convert waste heat into electricity and may have a significant impact on future electrical power generation. For a good thermoelectric material, it must have a high Seebeck coefficient (*S*), a low electrical resistivity (*R*), and a low thermal conductivity (*k*). The thermal conductivity of thin films is difficult to measure, therefore, the thermoelectric power factor ($P_F = S^2/R$) is usually used to characterize the thermoelectric properties. In recent years, a great progress has been made in reduction of thermal conductivity by using the concept of nano-structure in bulk materials [1–10]. The nano-structure introduces numerous interfaces in the materials which can effectively scatter the medium- and long-wavelength phonons and thus reduce the heat conduction. These interfaces, however, also increase the carrier scattering and thus adversely affect the carrier mobility. As a result, the electrical resistivity is usually increased. Due to the difficulty in making the grain as small as several nanometers, the quantum confinement effect or the enhancement of Seebeck coefficient has been seldom observed in nano-structured bulk materials [3]. Although a significant decrease in electrical resistivity was observed in Bi_2Te_3 bulk materials with layered nano-structure, the Seebeck coefficient was also decreased [4]. It is very difficult to increase the Seebeck coefficient with a simultaneous decrease in the electrical resistivity for conventional thermoelectric materials.

Many theoretical works have predicted that low-dimensional thermoelectric materials (for example, ultra-thin films) will have high Seebeck coefficient and low electrical resistivity [11–16]. Experimental observation of the enhancement of the Seebeck coefficient has been reported in Si/Ge, $SrTiO_3/SrTiO_3$:Nb, and PbTe/

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http://dx.doi.org/10.1016/j.matchemphys.2014.03.035
0254-0584/

PbTe:Eu nano-scale thin films [17–21]. But the electrical resistivity was not changed as compared with the bulk value of $SiTiO_3$:Nb for the $SiTiO_3/SrTiO_3$:Nb thin film [18,19]. Among the thin films of PbTe/PbTe:Eu, only one sample was reported to have a lower electrical resistivity [21]. A decrease in the electrical resistivity was observed in $CrSi_2$/Si thin films, but the Seebeck coefficient was not reported [22].

In this paper, a method of layer-by-layer deposition of $MnSi_{1.7}$ film by magnetron sputtering is reported. During the $MnSi_{1.7}$ film deposition, the deposition process is interrupted by closing the shutter for several minutes and then continues. Therefore, the $MnSi_{1.7}$ film consists of two sub-layers for one interruption, three sub-layers for two interruptions, and so on. It is found that the $MnSi_{1.7}$ film with two sub-layers has a higher Seebeck coefficient and a lower electrical resistivity as compared to the film without interruption.

2. Experimental

$MnSi_{1.7}$/Si and $MnSi_{1.7}$ thin films were deposited on glass, quartz, and thermally oxidized silicon substrates at high substrate temperature (either 723 K or 843 K) by magnetron sputtering of $MnSi_x$ ($x = 1.85, 2$) and Si targets. The magnetron sputtering system was equipped with four independent sputtering guns and the schematic diagram was reported previously [23,24]. The thickness of the silicon dioxide (SiO_2) layer on the thermally oxidized silicon substrate was 450 nm. The purities of the $MnSi_x$ and Si targets were 99.5 and 99.99 at.%, respectively. The base pressure of the vacuum chamber was approximately 6.3×10^{-4} Pa. An argon gas pressure of 0.35–0.75 Pa was maintained during the film deposition. The sample holder was rotated during the film deposition, therefore, the sample was homogeneous along the sample length direction. Three sets of samples, totaling nine samples, N1, N2, P1, P3, P5Q, P10Q, P1M, P2M, P3M, were prepared to investigate the influence of the number of sub-layers on the Seebeck coefficient and electrical resistivity of $MnSi_{1.7}$ films. The capital letters N and P represented that the $MnSi_{1.7}$ films were n- and p-type, respectively. The number after the capital letter indicated the number of sub-layers in the $MnSi_{1.7}$ film. The capital letter Q indicated that the substrate was quartz. The capital letter M denoted that a silicon layer doped with Al and Cu was grown on the $MnSi_{1.7}$ film for modulation doping [25,26].

The first set of samples consisted of two samples, N1 and N2. As shown in Fig. 1 schematically, (a) sample N1 had only one $MnSi_{1.7}$ layer while (b) sample N2 had two $MnSi_{1.7}$ sub-layers. But the total $MnSi_{1.7}$ film thickness was the same for the two samples, 175 nm. The substrate was SiO_2/Si and at a temperature of 843 K. A silicon intermediate layer with a thickness of 131 nm was first deposited to enhance the $MnSi_{1.7}$ film adhesion and also provide enough silicon for the $MnSi_{1.7}$ phase formation. The $MnSi_{1.7}$ layer was deposited on the silicon layer by sputtering a $MnSi_{1.85}$ target. For sample N2, the $MnSi_{1.7}$ layer deposition was interrupted for 3 min by closing the shutter during the deposition process, causing the formation of two $MnSi_{1.7}$ sub-layers. A silicon cap layer with a thickness of 20 nm was deposited on the top surface of the second $MnSi_{1.7}$ sub-layer. Finally, samples N1 and N2 were thermally annealed at 923 K for 40 min in another high vacuum chamber ($\sim 10^{-3}$ Pa) for the complete formation of $MnSi_{1.7}$ phase [24].

The second set of samples included three samples, P1M, P2M, and P3M. As shown in Fig. 2 (a) schematically for sample P1M, a $MnSi_{1.7}$ layer with a thickness of 25 nm was deposited on glass substrate at 723 K by sputtering a $MnSi_2$ target. Then an Al and Cu doped silicon layer with a thickness of 84 nm was deposited on the $MnSi_{1.7}$ layer at 723 K for modulation doping [25,26]. Analogous to sample N2, sample P2M had two $MnSi_{1.7}$ sub-layers as shown in

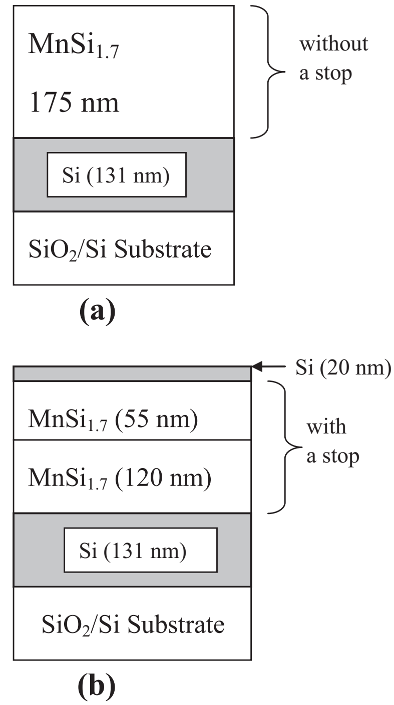

Fig. 1. Schematic diagrams of the deposition of n-type $MnSi_{1.7}$ films (a) without a stop (only one $MnSi_{1.7}$ layer, sample N1) and (b) with a stop of deposition for 3 min (two $MnSi_{1.7}$ sub-layers, sample N2). A $MnSi_{1.85}$ target is used for sputtering.

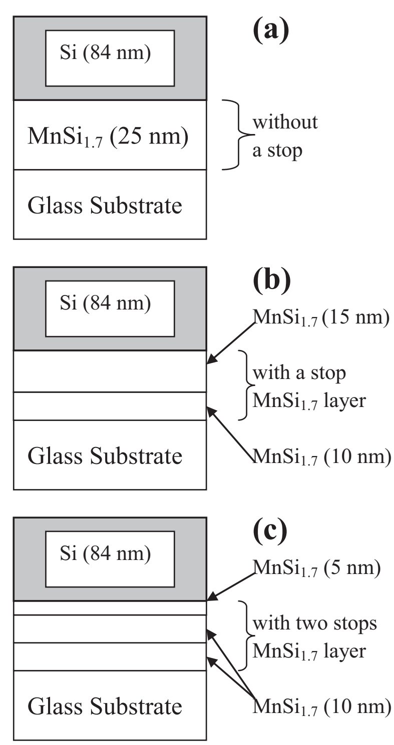

Fig. 2. Schematic diagrams of the Al and Cu modulation doped p-type $MnSi_{1.7}$ films (a) without a stop (only one $MnSi_{1.7}$ layer, sample P1M), (b) with a stop for 1 min (two $MnSi_{1.7}$ sub-layers, sample P2M), and (c) with two stops of deposition (three $MnSi_{1.7}$ sub-layers, sample P3M). A $MnSi_2$ target is used for sputtering.