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The effects of diffusion barrier layers on the microstructural and electrical properties in $CoSb_3$ thermoelectric modules

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ABSTRACT

We report the microstructure and electrical properties of $CoSb_3$ legs on which Au, Pt, and Ti are deposited by ultra-high-vacuum (UHV) radio frequency (RF) sputtering. After annealing, an intermetallic compound (IMC) layer, approximately 320 nm thick, forms at the interface of $CoSb_3$/Ti. This layer plays a significant role as a diffusion barrier in a $CoSb_3$ thermoelectric (TE) module. The IMC layer has little effect on the electrical properties of $CoSb_3$/Ti. However, no IMC layers were observed in $CoSb_3$/Au and $CoSb_3$/Pt, where Au and Pt diffused into the $CoSb_3$ leg to a great depth. Our results demonstrate that a Ti layer on a $CoSb_3$ leg deposited by a sputtering system is effective to form the IMC layer, preventing further diffusion of Ti and giving rise to enhance the efficiency of $CoSb_3$ TE modules.

1. Introduction

Thermoelectric modules (TE) have attracted considerable interest as next-generation power generators because of their high reliability, fast response, and lack of noise or pollution. The conversion efficiency in a thermoelectric cell strongly depends on the materials comprising the electrodes and thermoelectric materials [1,2]. $CoSb_3$-based skutterudites are among the most promising candidate materials for intermediate operating temperatures (600–900 K) in TE modules because of their high thermoelectric performance, mechanical stability, and high reliability. $CoSb_3$-based skutterudites are easily fabricated and can be p-type or n-type thermoelectric semiconductors, depending on the doping element [1–5]. However, the properties of the interface between metal electrodes and $CoSb_3$ pose challenges such as high interfacial resistance, high electrical resistance, mechanical instability, and thermal resistance, which decrease the efficiency of thermoelectric cells [6–9]. An alternative approach to creating diffusion barrier layers uses foils of Ti [10–13], Mo [14], CrSi [15], or Ni [15]; this is not only to prevent interdiffusion between the $CoSb_3$ and electrode materials but also to improve the electrical conductivity and mechanical properties of the junctions, to ultimately enhance conversion performance and operating reliability.

Here we have investigated the performance of Au, Pt, and Ti as diffusion barrier layers, with a ~2.5-μm-thick-layer of each metal is deposited by a DC sputtering method on the $CoSb_3$ leg and the microstructural and electrical properties of the composite are measured. Using this approach, it is possible to identify the material that forms an optimal diffusion barrier layer for $CoSb_3$-based TE modules. We discuss the effects of the diffusion barrier layer on the $CoSb_3$ modules' microstructure and electrical properties, which are crucial factors that determine their efficiency.

2. Experiment

Diffusion barrier layers of Au, Pt, and Ti thin films were deposited on $CoSb_3$ legs via ultra-high vacuum (UHV) radio frequency (RF) sputtering. Before deposition, the chamber pressure was kept in the range of 2×10^{-6} Torr during the pre-baking step. Deposition of the diffusion barrier layers was carried out under a constant Ar flow rate of 30 sccm at a RF power of 50 W, employing highly pure Au, Pt, and Ti targets (purity: 99.99%, 99.9%, and 99.9%, respectively) and Ar gas (purity: 99.9999%). Each diffusion barrier layer was approximately 2.5 μm thick. The $CoSb_3$ thermoelectric legs were fabricated by induction melting and spark plasma sintering (SPS) of high-purity Co (99.95%) and Sb (99.999%), which were reacted in stoichiometric proportion. More details can be found elsewhere [10].

The deposited Au, Pt, and Ti layers on the $CoSb_3$ thermoelectric legs were annealed at 773, 823, and 923 K for 24 h in vacuum, respectively. For the electrochemical cells, Pt current collectors were deposited by sputtering on both sides of

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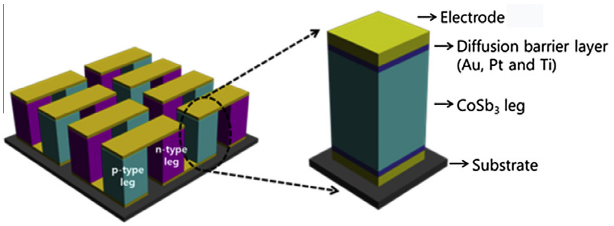

Fig. 1. Schematic diagram of a single cell composed of electrodes, diffusion barrier layers, a $CoSb_3$ leg, and substrate in a thermoelectric module.

the samples. The effective area of both electrodes was 0.78 cm^2. To investigate the microstructure of the samples, the diffusion barrier layers after annealing were examined by scanning electron microscopy (SEM; JSM7001F, JEOL Ltd.) and energy dispersive spectrometry (EDS; AZtec Energy, Oxford Instruments). The electrochemical impedance spectra (EIS) were measured with an electrochemical workstation (IM6eX, Zahner-elektrik GmbH & Co., KG) in the frequency range of 1–10 MHz, at an amplitude of 50 mV.

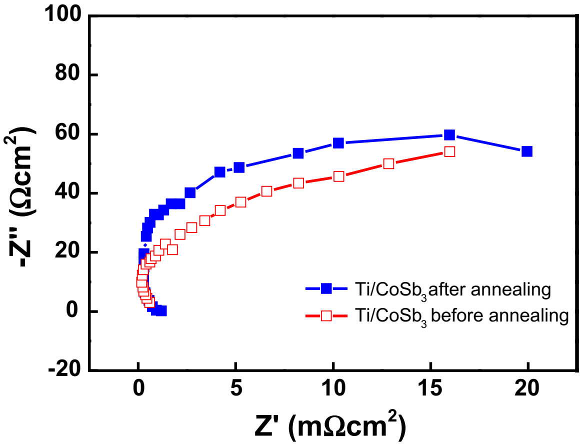

Fig. 4. Nyquist plots of AC impedance of Ti layer deposited on $CoSb_3$, before and after annealing.

3. Results and discussion

Fig. 1 shows a schematic diagram of a typical thermoelectric module consisting of eight pairs of both p- and n-type doped semiconductor materials, which are connected electrically in series and thermally in parallel. A single cell is composed of electrodes, diffusion barrier layers, and the $CoSb_3$ leg. Generally, a proper junction between the electrode and $CoSb_3$ is important for fabricating TE devices due to mutual diffusion of the elements. In our case, the samples were made of thick $CoSb_3$ thermoelectric legs with Au, Pt, and Ti diffusion barrier layers.

Fig. 2 displays cross-sectional SEM images with the EDS line scan profiles for the interfaces of $CoSb_3$/Au and $CoSb_3$/Pt, taken after annealing at 773 and 823 K for 24 h, respectively. Although the image shows no Au film in $CoSb_3$/Au due to evaporation of Au during annealing, the EDS profiles reveal that Au diffused into

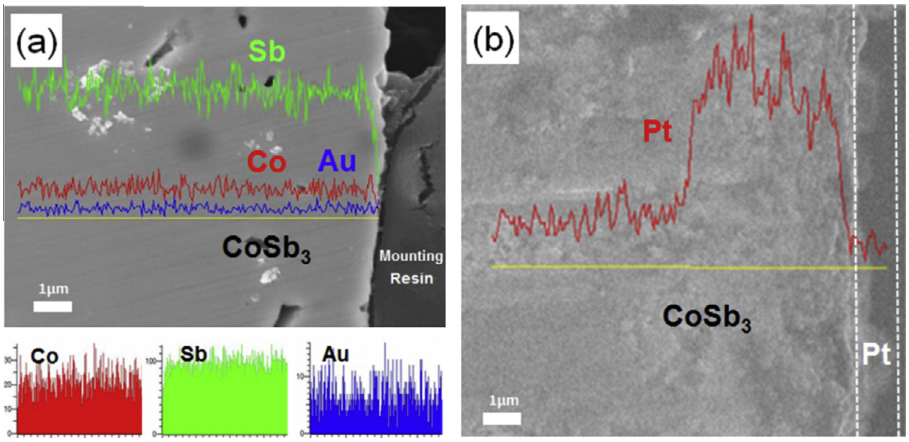

Fig. 2. Cross-sectional SEM images and EDS line scans of (a) Au and (b) Pt thin films deposited on $CoSb_3$ and annealed.

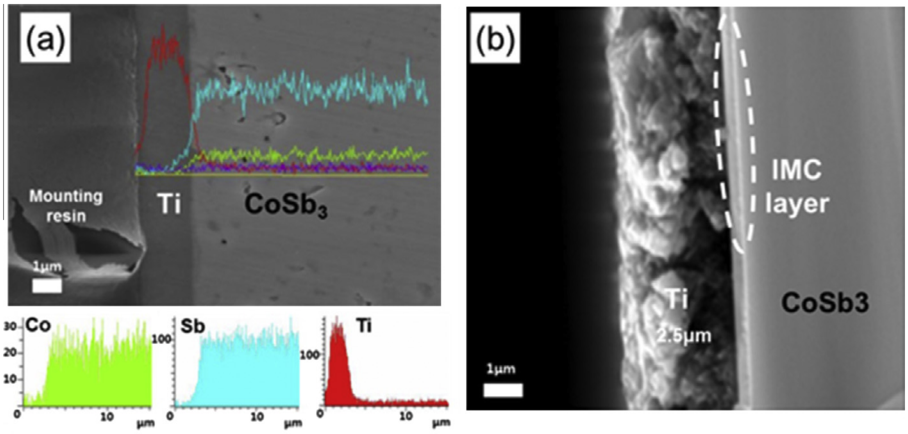

Fig. 3. Cross-sectional SEM images of Ti layer deposited on $CoSb_3$ and annealed.

the $CoSb_3$ leg, as shown in Fig. 2(a). The diffusion depth is larger than 7 μm. The EDS profiles in Fig. 2(b) also show that Pt diffused into the $CoSb_3$ leg; however, the Pt film appears to be peeled off because of poor adhesion to $CoSb_3$.

In order to investigate the performance of the Ti layer as a diffusion barrier, cross-sectional SEM images of $CoSb_3$/Ti after annealing at 923 K for 24 h were taken (Fig. 3). Although EDS profiles indicate that Ti diffused into the $CoSb_3$ leg, as shown in Fig 3(a), we found that the diffusion depth of Ti is approximately 0.5 μm, much smaller than that of Au. The SEM image in Fig. 3(b) provides further detail on the diffusion depth of Ti, showing a 2.5-μm-thick Ti layer with a 320-nm-thick interface layer on $CoSb_3$. A previous study identified such a layer between $CoSb_3$ and Ti, calling it the intermetallic compound (IMC) layer [13]. The IMC layer originates from the difference in chemical potential between Co and Ti, leading to their mutual diffusion. Previous reports have indicated that the reliability of $CoSb_3$/Ti/Mo–Cu devices is maintained up to an IMC layer thickness of 20 μm. Our IMC layer in $CoSb_3$/Ti is about 20 times thinner compared to that of $CoSb_3$ with a Ti foil deposited by SPS [13]. We infer that our method forms a more effective diffusion barrier layer compared to the SPS deposition of Ti foil onto $CoSb_3$, since our method allows for slower growth of the IMC layer during annealing.

To confirm the effect of a diffusion barrier layer on the electrical properties of $CoSb_3$/Ti, Fig. 4 presents Nyquist plots of EIS data measured for the Ti layer deposited on the $CoSb_3$ leg before and after annealing. Typically, a single arc at high frequency response can be attributed to an equivalent circuit with a resistor parallel to a capacitor [16]. The overall resistance of the Ti layer on the $CoSb_3$ leg after annealing as illustrated in Fig. 4 shows an increase (20.05 $m\Omega\,cm^2$) compared to that of the one before annealing (16.09 $m\Omega\,cm^2$). Our results indicate that the formation of the IMC layer at the $CoSb_3$/Ti interface has little effect on the electrical properties of $CoSb_3$/Ti.

4. Conclusions

We have investigated the effects of a diffusion barrier layer on the microstructure and electrical properties of $CoSb_3$-based thermoelectric modules. We deposited 2.5-μm-thick layers of Au, Pt, and Ti on a $CoSb_3$ leg using UHV RF sputtering. SEM reveals that an IMC layer approximately 320 nm thick s formed at the interface of $CoSb_3$/Ti after annealing. This layer has little effect on the electrical properties of $CoSb_3$/Ti, but plays a significant role as a diffusion barrier in $CoSb_3$ TE modules. On the other hand, Au and Pt diffuse to a great extent into $CoSb_3$, and thus $CoSb_3$/Au and $CoSb_3$/Pt do not exhibit an IMC layer. Our results suggest that depositing a Ti thin layer onto $CoSb_3$ via sputtering forms an IMC layer at the $CoSb_3$/Ti interface, enhancing the efficiency of $CoSb_3$ TE modules.

Acknowledgments

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References

[1] B.C. Sales, D. Mandrus, R.K. Williams, Filled skutterudite antimonides: a new class of thermoelectric materials, Science 272 (1996) 1325–1328.
[2] K.H. Kim, J.S. Park, J.P. Ahn, Joining and properties of electrode for $CoSb_3$ thermoelectric materials prepared by a spark plasma sintering method, J. Korean Cryst. Growth Cryst. Technol. 20 (2010) 30–34.
[3] G.S. Nolas, J.L. Cohn, G.A. Slack, Effect of partial void filling on the lattice thermal conductivity of skutterudites, Phys. Rev. B 58 (1998) 164–170.
[4] X.F. Tang, L.M. Zhang, R.Z. Yuan, L.D. Chen, T. Goto, T. Hirai, W. Chen, C. Uher, High-temperature thermoelectric properties of n-type $Ba_yNi_xCo_{4-x}Sb_{12}$, Mater. Res. 16 (2001) 3343–3346.
[5] A. Muto, J. Yang, B. Poudel, Z. Ren, G. Chen, Skutterudite unicouple characterization for energy harvesting applications, Adv. Energy Mater. 3 (2013) 245–251.
[6] M.S. El-Genk, H.H. Saber, T. Caillat, Efficient segmented thermoelectric unicouples for space power applications, Energy Convers. Manage. 44 (2003) 1755–1772.
[7] T. Shimozaki, K.S. Kim, T. Iwata, T. Okino, C.G. Lee, A resistance ratio analysis for $CoSb_3$-based thermoelectric unicouples, Mater. Trans. 43 (2002) 2609–2616.
[8] T. Caillat, J.P. Fleurial, G.J. Snyder, A. Zoltan, D. Zoltan, A. Borshchevsky, A new high efficiency segmented thermoelectric unicouple, Intersoc. Energy Convers. Eng. Conf. 34 (1999) 2567–2570.
[9] D. Zhao, C. Tian, S. Tang, Y. Liu, L. Jian, L. Chen, Fabrication of a $CoSb_3$-based thermoelectric module, Mater. Sci. Semicond. Process. 13 (2010) 221–224.
[10] S.M. Choi, K.H. Kim, S.M. Jeong, H.S. Choi, Y.S. Lim, W.S. Seo, I.H. Kim, A resistance ratio analysis for $CoSb_3$-based thermoelectric unicouples, J. Electron. Mater. 41 (2012) 1004–1010.
[11] X. Li, L. Chen, J. Fan, S. Bai, Mo/Ti/$CoSb_3$ joining technology for $CoSb_3$ based materials, ICT (2005) 528–530.
[12] J.F. Fan, L.D. Chen, S.Q. Bai, X. Shi, Joining of Mo to $CoSb_3$ by spark plasma sintering by inserting a Ti interlayer, Mater. Lett. 58 (2004) 3876–3878.
[13] D. Zhao, X. Li, L. He, W. Jiang, L. Chen, High temperature reliability evaluation of $CoSb_3$/electrode thermoelectric joints, Intermetallics 17 (2009) 136–141.
[14] K.T. Wojciechowski, R. Zybala, R. Mania, High temperature $CoSb_3$–Cu junctions, Microelectron. Reliab. 51 (2011) 1198–1202.
[15] J.K. Lee, S.M. Choi, W.S. Seo, Thermoelectric properties of the Co-doped n-type $CoSb_3$ compound, J. Korean Phys. Soc. 57 (2010) 1010–1014.
[16] E. Barsoukov, J.R. Macdonald, Impedance Spectroscopy, Wiley, Boboken, 2005.