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Protective properties of YSZ/Ti film deposited on $CoSb_3$ thermoelectric material

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ABSTRACT

The YSZ (yttria-stabilized zirconia)/Ti film was deposited on $CoSb_3$ substrate by magnetron sputtering to suppress the sublimation of antimony in $CoSb_3$ during thermal aging test. Both YSZ and Ti film were columnar crystal. The YSZ film typically grew on Ti film in the island mode. No cracks, porosity or other defects were observed on YSZ film. The weight loss per unit area of $CoSb_3$ samples coated with YSZ/Ti film was much lower than that of uncoated $CoSb_3$ sample after accelerated thermal aging test. The results indicated that the sublimation of antimony in $CoSb_3$ was effectively suppressed by YSZ/Ti film.

1. Introduction

Thermoelectric (TE) material has attracted worldwide attention for their potential application in electronic cooling, waste heat recovery and special power generation [1–3]. The thermoelectric conversion efficiency depends on the material's dimensionless figure of merit *ZT*, defined as $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the total thermal conductivity, and *T* is the absolute temperature. Binary $CoSb_3$ skutterudite compound crystallizes in a body-centered cubic structure and has two interstitial voids at the 2*a* positions in the crystal lattice. Introducing foreign atoms into these voids to act as strong phonon scattering centers could greatly reduce the lattice thermal conductivity of $CoSb_3$ compound, and thus enhance the TE properties of $CoSb_3$-based skutterudites. High *ZT* values have been reported for both *p*- and *n*-type single-filled skutterudite materials. Therefore $CoSb_3$-based skutterudites are regarded as one of the most promising TE materials operating at elevated temperature [4–6]. However, a key issue for $CoSb_3$-based skutterudites in application is the sublimation of antimony from the TE materials, especially close to the hot-sides. Such sublimation could change the composition of skutterudites and degrade the performance of TE unicouples over time [7,8]. In addition, the sublimation products can condense on the cold-side of the TE unicouples, leading to the electrical short circuit of TE device. In other words, the degradation of $CoSb_3$-based skutterudites serving at high temperature under the circumstance of vacuum or inert atmosphere mostly results from the sublimation of antimony [9,10]. Therefore, developing a protective coating to suppress the sublimation of antimony is essential for the application of $CoSb_3$-based skutterudites.

So far, few studies about the coating or protective film for $CoSb_3$-based skutterudites were reported. Cr-5Si thin film deposited on $CoSb_3$ by magnetron sputtering was used to prevent the degradation of skutterudites at high temperature in air, but the thin film lost the protection function at 600 °C [11]. Dong et al. developed the silica-based composite coatings on the surface of *n*-type $Yb_{0.3}Co_4Sb_{12}$ and *p*-type $CeFe_3CoSb_{12}$ skutterudites by using hybrid silica sol as raw material [12], whereas the method is complex and difficult to control the thickness of film. In brief, the aim of coating on $CoSb_3$-based skutterudites is to suppress the sublimation, or at least reduce it to an acceptably low level. In our previous studies, Ti film was deposited on the $CoSb_3$ material using magnetron sputtering [13]. The results showed that Ti film is compatible with $CoSb_3$ substrate and can reduce significantly the loss of antimony at high temperature. However, the electric current circulation in the metallic Ti film can effectively increase the current flowing in the coated part of hot sides, increasing Joules losses and thus, decreasing the conversion efficiency of $CoSb_3$-based skutterudites. Additionally, the larger thermal shunting of metallic Ti film on $CoSb_3$-based skutterudites can also weaken the performance of TE device. Therefore the metallic Ti film should be as thin as possible in order to minimize these effects. Preferably, the coating should have low electrical conductivity and thermal conductivity as well as a comparable coefficient of thermal expansion (CTE)

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with $CoSb_3$ thermoelectric material. YSZ material has low electrical and thermal conductivity [14–16]. In addition, the CTE of YSZ can be adjusted to match with that of $CoSb_3$. The CTE of $CoSb_3$ and YSZ (6% mol Y_2O_3 stabilized ZrO_2) is $(\sim0.92–1.05) \times 10^{-5}\,K^{-1}$ and $(\sim0.90–0.99) \times 10^{-5}\,K^{-1}$ when temperature ranges from 100 °C to 600 °C, respectively. Therefore, 6% mol Y_2O_3 stabilized ZrO_2 was selected as YSZ target and YSZ film is possibly an appropriate protective coating for $CoSb_3$ material.

In this study, the YSZ/Ti film was conveniently deposited on $CoSb_3$ substrate by magnetron sputtering to prevent the sublimation of antimony during thermal aging test. The microstructure and growth feature of YSZ on Ti film was observed using SEM. As the $CoSb_3$-based generator generally works at about 500 °C, the accelerated thermal aging tests were carried out at 650 °C for 24 h. The effects of YSZ/Ti film on suppressing the sublimation of antimony were evaluated by thermogravimetic analysis and measuring the TE properties of $CoSb_3$ after accelerated thermal aging test in vacuum. Related thermal aging behavior was discussed. The results are expected to be beneficial to the construction of $CoSb_3$-based TE device.

2. Experimental details

The substrate material, $CoSb_3$, was synthesized by melting, quenching, and annealing process. Stoichiometric quantities of the constituent pure elements Co (99.99%, powder) and Sb (99.99%, powder) were weighed according to the mole ratio, loaded in a quartz tube with carbon depositing on the inner wall, and sealed under a pressure of 0.05 Pa. The samples were melted at 1050 °C for 16 h and then was quenched in saltwater. The obtained solid product was ground into fine powder and then densified into disks with 10 mm in diameter and 2 mm in thickness by hot-pressing (HP) sintering at 570 °C for 40 min in a graphite die. The relative densities of $CoSb_3$ samples measured were higher than 98%. Then the 8 mm × 6 mm × 2 mm rectangles were cut from the $CoSb_3$ disks. All surfaces of $CoSb_3$ samples were metallographically polished down to 1 μm diamond paste. Before being place in the deposition chamber, the $CoSb_3$ substrates were first ultrasonically cleaned in acetone for 10 min, and then were dried by blowing hot air.

Direct current (DC) and radio frequency (RF) magnetron sputtering were used to deposit Ti film and YSZ film on $CoSb_3$ substrate by means of a specially designed magnetron sputtering system, respectively. The size of titanium and YSZ target is φ74 mm × 3 mm (Ti: 99.99%, YSZ: 99.98%, 30.1 at.% Zr, 3.8 at.% Y and 66.1 at.% O, Beijing Haipu Technology Co., Ltd). During DC sputtering, the target-to-substrate distance was 70 mm. The substrate temperature was 200 °C. The flow rate of the argon (99.99% purity) was 50 standard cubic centimeter per minute (sccm). Pre-sputtering of the Ti target was performed for 3 min before each deposition. The DC deposition time of each sample was 15 min. Then the YSZ film was deposited on the Ti film using RF sputtering. In the process of RF sputtering, the total working pressure, substrate temperature and power supplied to the target was 0.2 Pa, 200 °C and 300 W, respectively. By adjusting the deposition time, the thickness of YSZ film was controlled. The pulse parameters of RF magnetron sputtering in the present study are given in Table 1.

The structural property of YSZ film was characterized by X-ray diffraction (XRD, Rigaku, Rint-2000). The surface morphology of YSZ film on $CoSb_3$ substrate was observed by field emission SEM (JEOL, JSM-6700F). The film thickness was measured by a Dektak profilometer and the precision is of the order of 5%. The weight and surface area of $CoSb_3$ substrates were measured before each test. The weight loss divided by exposed surface area provided the weight loss per unit area. The size of $CoSb_3$ substrate was 8 mm × 8 mm × 4 mm. It should be noted that the six surfaces of $CoSb_3$ substrate were all coated with Ti/YSZ film. The $CoSb_3$ samples with YSZ/Ti film were placed inside quartz tube and sealed under vacuum (0.05 Pa) after 5 times Ar evacuation. Then the quartz tube was heated to the accelerated aging temperature (650 °C) at a rate of 220 °C/h in the furnace. After keeping at the aging temperature for 24 h, the samples were cooled to room temperature in furnace naturally. The mass changes were calculated by the difference after and before the thermal aging tests from an electronic balance with an accuracy of 0.1 mg. Seebeck coefficient and electrical conductivity of $CoSb_3$ samples after thermal aging test were measured by the standard four-probe method (ULVAC-RIKO, ZEM-2) in a flowing Ar atmosphere. Thermal conductivity was measured by a laser flash method (NETZSCH, LFA427) in vacuum. As the direction of thermal fluid and current flow is parallel with that of coating in the TE device, the electrical conductivity and Seebeck coefficient of $CoSb_3$ samples with coating on four side faces were measured. The coatings on the end surfaces of bar samples were polished and removed. Based on the same TE device model, the coatings on the upper surface and bottom surface of $CoSb_3$ specimens were polished and removed for the thermal conductivity test. The detailed thermoelectric measurements of $CoSb_3$ samples coated with film were described in our previous study [13]. All measurements were performed in the temperature range of 27–550 °C.

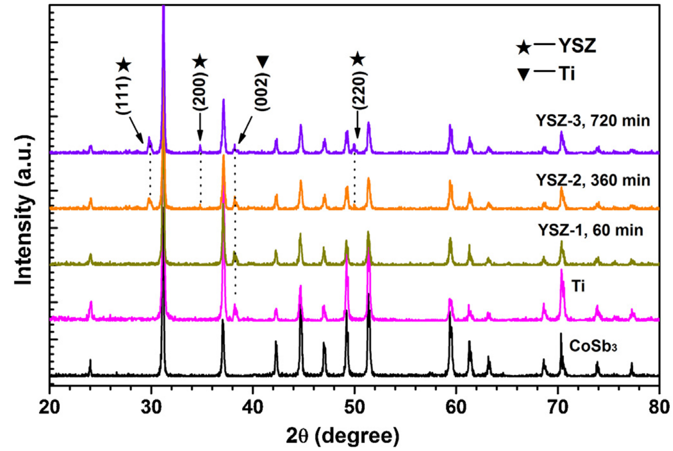

Fig. 1. XRD patterns of the as-deposited Ti and YSZ/Ti films (30, 360 and 720 min) on $CoSb_3$ substrate.

3. Results and discussion

The XRD patterns of YSZ/Ti films on $CoSb_3$ substrate deposited by different time are shown in Fig. 1. Compared with the peaks of uncoated $CoSb_3$ sample, the peak of Ti (0 0 2) at 38.4° can be observed in the XRD pattern of Ti/$CoSb_3$ sample. As the deposition time of RF magnetron sputtering was 60 min, no obvious peak of

Table 1
Deposition conditions of YSZ film on Ti/$CoSb_3$ samples prepared by RF magnetron sputtering.

YSZ film	Base pressure (mPa)	Working pressure (Pa)	Power (W)	Time (min)	Temperature (°C)	Thickness (μm)	Composition
YSZ-1	2.2	0.2	240	60	200	–	–
YSZ-2	2.2	0.2	240	360	200	1.1	$Zr_{0.85}Y_{0.15}O_{1.93}$
YSZ-3	2.2	0.2	240	720	200	2.6	$Zr_{0.85}Y_{0.15}O_{1.93}$