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Design of diffusion barrier and buffer layers for β-Zn_4Sb_3 mid-temperature thermoelectric modules

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ABSTRACT

The purpose of this work was to investigate the feasibility of using sputtered Ti/W-Ti/Ti multilayer as diffusion barrier and buffer layers between β-Zn_4Sb_3 thermoelectric (TE) material and Ag interconnect layer for mid-temperature TE module applications. Interdiffusion at the interface was examined by both scanning electron microscope and Auger electron spectroscopy. After penetrating the Ti buffer layer, Ag, Zn and Sb were successfully blocked by the W-Ti diffusion barrier layer. We also proved that the TE sample with diffusion barrier and buffer layers showed phase stability after high temperature aging. Also, the sheet resistance decreased as the temperature increased and it indicated good electrical properties at high working temperatures. In addition, the solid-liquid interdiffusion method was used to join the TE module, and the bonding remained stable at the TE module working temperature.

1. Introduction

As the public awareness in environmental issues has arisen in recent years, the applications of thermoelectric (TE) modules are becoming widespread for reducing fuel consumption. TE materials convert temperature difference into electrical power through Seebeck effect [1,2]. The conversion efficiency depends on their TE figure of merit (ZT), which can be expressed as $ZT = S^2T\sigma/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity and T is average temperature of the hot and the cold plates of the TE module. TE materials are normally classified depending on their temperature ranges of applications. The mid-temperature range is from 200 to 600 °C, which is the temperature range of most industrial waste heat sources [3–8]. Among the wide variety of mid-temperature materials, Zn-Sb system is promising due to its low toxicity and low-cost for fabrication [9]. Specifically, β-Zn_4Sb_3 in this system is stable at room temperature, while it would transfer to ZnSb and Zn due to Zn diffusion during fabrication and transfer back to β-Zn_4Sb_3 when the temperature is above 250–300 °C [10]. Nevertheless, because β-Zn_4Sb_3 has quite low thermal conductivity close to the amorphous limit of below 1 W/mK [11], it possesses a high value of ZT and is worth exploring [12]. However, to make the module functional, the joint between the electrodes and the TE material is another critical issue in addition to the ZT value [13,14].

Generally, traditional soldering was used in dealing with TE joint because the low bonding temperature could prevent thermal cracking during the bonding process [15]. However, the highest operating temperature of TE was limited by the melting point of the solder and soldered TE modules might break down when the working temperature was higher than the melting point of the solder alloy. The optimized operating temperature for the application of β-Zn_4Sb_3 is 400 °C where β-Zn_4Sb_3 possesses the highest ZT value at this temperature [3,5,16–18]. Hence, brazed TE module was of concern because of its melting point while it might result in serious interfacial cracking during solidification of the brazed filler [19]. Currently, spark plasma sintering [20] is the most common way for the joint between TE material and metallic electrodes working in the medium and high temperature ranges to prevent interfacial cracking. However, the high heating rate during the spark plasma sintering would degrade the intrinsic property of mid-temperature β-Zn_4Sb_3. Therefore, spark plasma sintering was not suitable for the β-Zn_4Sb_3 module [21]. In addition to bonding, another issue could occur; i.e., the interdiffusion between the TE material and solder could degrade the device performance because the carrier concentration of the TE material would be changed. The same diffusion problem also occurred in other TE system; e.g.,

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Bi_2Te_3 TE material with In-based solder [13]. Hence, successful joints for TE modules should satisfy both low interdiffusion and good adhesion in the TE system.

To resolve the diffusion problem, a diffusion barrier was required between electrodes and TE materials to enhance the joint reliability and device efficiency [14,22–25]. Thin film metallic glass [26–29] has been adopted as diffusion barrier between Si and Cu [27] and between Cu and Sn [29] in recent years due to its amorphous structure that could efficiently impede diffusion. However, it was found that some element in metallic glasses such as Ni would interact with Zn in β-Zn_4Sb_3 to form Ni_5Zn_{21} intermetallic compound [30]. Hence, refractory elements, such as W and Ti, were considered as the diffusion barrier material in the present study. W-Ti thin films have many attractive properties from the industrial application point of view, such as low electrical resistance, high thermal stability, chemical inertness and good adhesion [31–33]. W-Ti has been commonly used as diffusion barrier [34–38]. Many studies have investigated W-Ti as a barrier layer for Ag, Cu and Al interconnects on Si wafers [35,39–42]. It was reported that W-Ti in contact with Ag, Cu and Al was stable up to 600 °C. However, no research has been performed on W-Ti as the diffusion barrier layer for TE systems.

In this study, an alternative joining technique of solid-liquid interdiffusion (SLID) [19], which was based on the principle of isothermal solidification and interfacial intermetallic reaction, was adopted to overcome the problem of thermal cracking to ensure that the mid-temperature TE module (β-Zn_4Sb_3) could be used under the optimized working temperature of 400 °C [19,43–45]. To resolve the issue of interfacial diffusion between the Ag interconnect layer and β-Zn_4Sb_3, W-Ti as a diffusion barrier layer was adopted in the present study. However, W-Ti film was found to be hard to bond to β-Zn_4Sb_3 in the present study and improvement of adhesion was required. During thin film deposition, Ti thin film has often been used as the adhesive layer [46,47]. Also, Ti has the coefficient of thermal expansion that is less than β-Zn_4Sb_3 and Ag but is higher than W-Ti, and it could mitigate thermal mismatch stresses in the system. Hence, Ti was adopted as the buffer layer in the present study to enhance adhesion between W-Ti layer and adjacent layers (i.e., β-Zn_4Sb_3 and Ag).

2. Material and methods

2.1. Processing of TE material and Ag interconnect with diffusion barrier and buffer layers

β-Zn_4Sb_3 source alloy ingot was obtained from Thermal Management Materials & Device Lab., Industrial Technology Research Institute (ITRI). The source ingot was processed by mechanical grinding with Al_2O_3 milling balls for 18 h and subsequently hot pressing under 60 MPa at 390 °C for 180 s to fabricate the TE bulk material. It was then cut into pieces with a dimension of $0.5 \times 0.5 \times 0.3$ cm^3 each. Prior to deposition of diffusion barrier and buffer layers, the TE materials were cleaned ultrasonically in acetone, ethanol and deionized water for 10 min each in sequence [48]. Small thicknesses of the TE materials were preferred for sputtering deposition of films because ion bombardment would be converted to heat that could not be readily released from TE material to the substrate holder due to the low thermal conductivity of β-Zn_4Sb_3. The chamber was pumped to the base pressure of 5×10^{-7} Torr before the deposition process. After the introduction of the sputtering gas (Ar 99.999%) into the chamber, the working pressure was kept at 4×10^{-3} Torr. The substrate holder was rotated at a speed of 60 rpm with the working distance of 10 cm to maintain uniformity of chemical composition of the coating. The vendor of our sputtering targets was Ultimate Materials Technology Co., Ltd., and W-Ti (30 at.% Ti), Ti (purity 99.99 wt.%) and Ag (purity 99.99 wt.%) targets of 7.6 cm in diameter were used in the three-target DC/RF sputtering system. Ti film of ~1 μm thickness was deposited first on the β-Zn_4Sb_3 TE material by DC magnetron sputtering at a power of 50 W for 4000 s. Then, W-Ti of ~1 μm thickness was deposited at a power of 50 W for 2000 s. After that, Ti was deposited again under the same condition as the first deposition of Ti film. The thickness of 15 μm was usually required for Ag interconnect layer used in SLID bonding process [19]. It would be impractical to deposit such a thick Ag layer using sputtering and electroplating was used instead. However, because of the poor adhesion between Ti film and electroplated Ag, 100 nm Ag was deposited on the top of Ti film by sputtering prior to electroplating. Finally, Ag was deposited by electroplating at a current of 0.02 A for 10 min.

2.2. Characterization of interdiffusion, phase stability and sheet resistance

At the joint interface, interdiffusion was analyzed by scanning electron microscope (SEM, JEOL, JSM-7800F Prime) equipped with energy dispersive spectroscopy (EDS). To examine diffusion across the interfaces in details, the compositional depth profile was obtained using the Auger electron spectroscopy (AES) equipped with an Ar-ion gun for etching. The etching condition was 30.3 nm/min by referring to the etching rate of SiO_2, and the signal collection time per cycle for the sample was 7 s. Because of the slow etching rate of the Ar-ion gun, reduced thickness of the sample was used for AES analyses. In this case, both Ti layers of ~40 nm thickness were

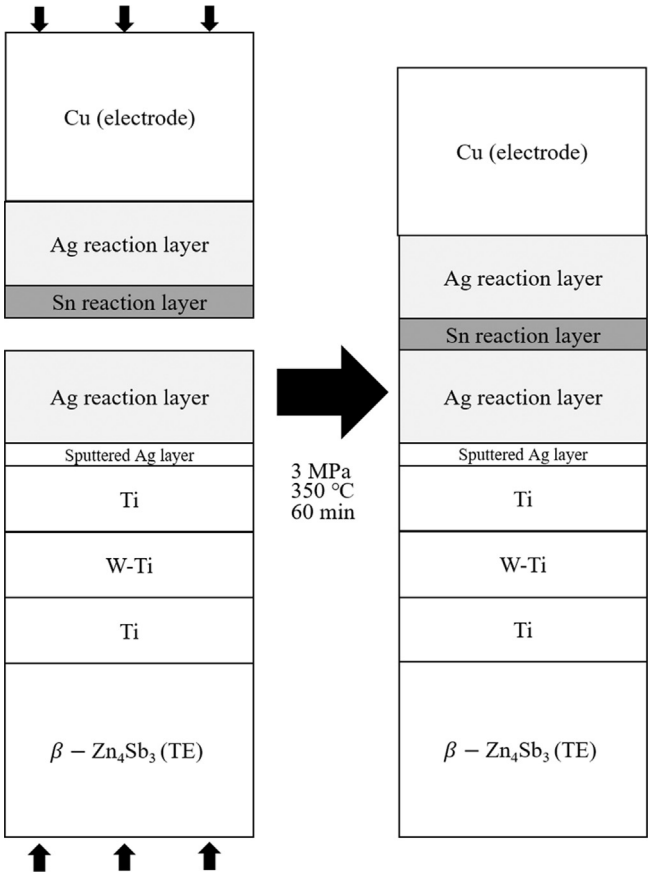

Fig. 1. Schematics showing the SLID joining process for manufacturing β-Zn_4Sb_3 TE module with Ag-based solder and Ti/W-Ti/Ti diffusion barrier and buffer layers.