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Electrically motivated atomic migration and defect formation in $Bi_{0.5}Sb_{1.5}Te_3$ compounds

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HIGHLIGHTS

- Current-induced Ag migration behavior in BST compounds were studied.
- The values of $D{\cdot}Z^*$ for Ag electromigration in BST was determined.
- The diffusion path and Ag-related charged defects in BST were identified.
- The electrical properties of BST were tuned by the current-induced doping process.

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ABSTRACT

Current-induced Ag migration behavior and defect formation mechanism in p-type $Bi_{0.5}Sb_{1.5}Te_3$ (BST) compounds are investigated. By applying an electric current of 170 A/cm^2 through a hot-pressed BST at 150 °C with one side attached to a thin Ag foil, Ag_2Te secondary phases precipitate first in the BST and decompose subsequently after extended current stressing time. Ag elements migrate in BST toward the cathode side with a $D{\cdot}Z^*$ product of 8×10^{-7} cm^2/s, where D and Z^* are diffusivity and electromigration effective charge number of Ag in BST, respectively. The van der Waals gap between two neighboring Te layers is identified to be the major path for Ag electromigration. Electrically motivated Ag atoms take Sb lattice sites eventually by forming Ag_{Sb} acceptor defects in BST. The electrical resistivity of current-stressed BST was lowered by one order of magnitude as a result of greatly increased carrier concentration. The study demonstrates a route of adjusting electrical properties of BST compounds through the current-induced doping process.

1. Introduction

Semiconducting V-VI compounds, especially $(Bi_xSb_{1-x})_2(Se_yTe_{1-y})_3$, have been extensively utilized in thermoelectric energy harvesting and solid-state cooling devices that operate at low temperatures. To improve conversion efficiency of thermoelectric devices, some fabrication strategies are exercised to optimize the interrelated Seebeck coefficient, electrical conductivity and thermal conductivity of featured thermoelectric materials [1,2]. For example, nanostructure engineering is applied to reduce lattice thermal conductivity [3], while defect engineering is essential for maximized thermoelectric power factor [4]. Doping of halogen or metallic elements is a common approach to tailor the thermoelectric properties of various telluride compounds [5–8]. It has been reported that Ag atoms tend to occupy Sb sites (Ag_{Sb}) and become electron acceptors in Sb_2Te_3, but take interstitial sites (Ag_i) in Bi_2Te_3 preferentially to serve as electron donors [9]. $Ag_xBi_{0.5}Sb_{1.5-x}Te_3$ ($x = 0.05–0.4$) has demonstrated higher thermoelectric power factor and lower lattice thermal conductivity than pristine $Bi_{0.5}Sb_{1.5}Te_3$ (BST) [8]. Conventionally, Ag atoms can be either incorporated into telluride compounds during crystal growth or driven into the crystal lattice through solid-state diffusion. Nevertheless, some secondary precipitates formed during high-temperature process may affect transport properties of Ag-doped telluride compounds.

Electrically-induced dopant migration in semiconductors has long been a subject of interest because it can change electronic properties as well as p-n junction profile of semiconductors [10]. It has been reported that Ag atoms are motivated easily in some p-type telluride compounds such as CdTe and $Cd_xHg_{1-x}Te$ under electrical stressing [11,12]. Moreover, electrically-induced

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precipitation of secondary phases has also been observed in bismuth telluride based compounds, e.g. Sb-rich precipitates in electrically stressed BST compounds [13]. An early investigation indicated that Ag, Au and Cu trace elements in single-crystal Bi_2Te_3 migrated from anode to cathode under a current density of 150 A/cm^2, but the migration direction was reversed when the current density was raised to 250 A/cm^2 and at the temperature above 400 °C [14]. The bipolar electromigration (EM) behavior was attributed to the presence of two types of dopant-related defects that were respectively activated in Bi_2Te_3 at different current density and temperature. The current-induced dopant migration may cause the change of transport properties of thermoelectric materials and affect the performance of thermoelectric generators operating at elevated temperature and high current density. In this study, we investigate the current-induced Ag migration behavior in p-type BST based on compositional analysis, crystal structure examination and electrical transport property measurement. The EM-induced drift velocity of Ag element in BST compounds was determined experimentally. The diffusion mechanism and electronic characteristics of Ag-related lattice defects in the electrically stressed BST were also discussed.

2. Experimental

Bi (99.99 wt.%, ADMAT), Sb (99.99 wt.%, ADMAT) and Te (99.99 wt.%, ADMAT) elements were weighted at an atomic ratio of 1: 3: 6 and sealed in an evacuated quartz ampule with extra 4 wt.% of Te. The additional Te is to compensate the possible Te loss during high-temperature process. The quartz ampoule was kept in a furnace at 850 °C for 24 h and turned upside down repeatedly during melting for compositional homogenization. The melt was solidified after water quenching from 850 °C. The solidified ingot was crushed and milled into small powders (<25 μm in size) using a planetary ball miller (PM-100, Retch). These fine powders were poured into a square stainless-steel mold (7 mm × 7 mm) with a ceramic insulating liner. The mold was loaded into a system that was designed for passing a high current through the sample during hot pressing. Firstly, the powders were pressed to form a densified bulk under a pressure of 50 MPa in N_2 ambient at 300 °C for 1 h. The relative density of the hot-pressed BST sample was measured to be 98 ± 1% using the Archimedes method. Next, we released one punch rod from the mold and inserted a thin Ag foil (99.98%, Nilaco) of 0.05 mm in thickness on the sample surface prior to reloading the punch rod back to the mold. The sample was heated to 150 °C under a pressure of 20 MPa followed by a gradual introduction of electric current from 0 to 170 A/cm^2 in 30 min. The slow current introduction process, namely the current-raising period, is to prevent the Joule-heating induced temperature overshoot in the pressed sample. Finally, a current-stressing testing was performed on the post current-raising sample at 150 °C under three different conditions: (1) no current applied; (2) Ag anode/BST at 170 A/cm^2; (3) Ag cathode/BST at 170 A/cm^2. The duration of current application ranged from 30 min to 8 h.

Ag concentration in the BST samples was measured by a field-emission scanning electron microscope (FE-SEM, SU8010, Hitachi) equipped with an energy dispersive spectrometer (EDS). The EDS measurement was taken with an imaged region of 80 μm × 60 μm on the sample. Each data point was averaged from five different measurements at a specific distance from the Ag/BST interface. The Ag concentration profile of the BST sample was thus determined by repeating the above measurements at different distance from the interface. Furthermore, an elemental mapping analysis on the BST samples was also carried out by electron probe microanalysis (EPMA, JXA-8800 M, JEOL). Crystal structure and lattice constant of the BST samples were determined by an x-ray diffractometer (XRD, D2 Phaser, Bruker) with the usage of Cu Kα line source. Electrical resistivity was measured by a typical four-point probe method. Carrier concentration and Hall mobility were measured at room temperature using a Hall effect measurement system (HMS-3000, ECOPIA) with a sensing current of 15 mA under a magnetic field of 0.55 T. It is noted that the Hall measurement samples were ground and thinned down to a thickness <120 μm for enhanced signal-to-noise ratio. Indium solders were melted at four corners of the specimen to minimize the contact resistance between BST and metal probes.

3. Results and discussion

Fig. 1 shows the Ag concentration profiles of the BST samples with and without introducing an electric current from 0 to 170 A/cm^2 at 150 °C in 30 min, respectively. The sample of no electric current applied reveals no marked Ag penetration into BST (Fig. 1(a)). However, the samples with the passage of electric current show gross Ag uptake by forming a stepped Ag profile in BST regardless of current polarity (Fig. 1(b)-(c)). The gross Ag uptake (~10 at %) is likely associated with the enhanced Ag diffusion in the vicinity of Ag/BST interface caused by the contact Joule heating. Since the Ag-doped BST exhibits a very low electrical resistivity as revealed later, the Joule heating would be mitigated and the gross Ag uptake is restricted within a limited region during the current-raising period. It is worth mentioning that the Ag-anode/BST sample exhibits slightly lower Ag concentration and longer diffusion tail than the Ag-cathode/BST sample. The different profiles suggests that Ag elements are prone to move toward cathode during the current-raising period. The current-induced Ag migration phenomenon is further supported by the subsequent current-stressing experiment. Two post current-raising BST samples with a

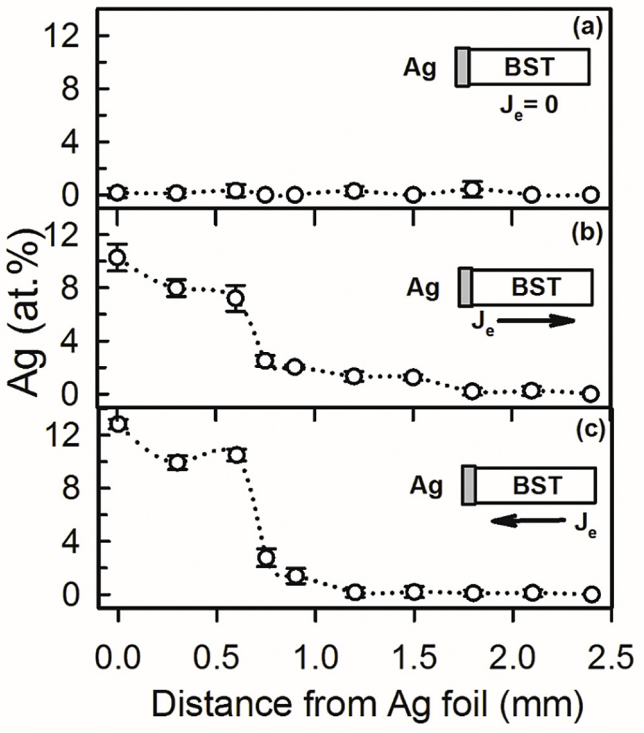

Fig. 1. Ag concentration profiles of the Ag/BST samples (a) annealed at 150 °C for 30 min without the passage of electric current; (b) Ag foil at anode and (c) Ag foil at cathode after raising the electric current from 0 to 170 A/cm^2 in 30 min at 150 °C.