Progress in Natural Science: Materials International xxx (xxxx) xxx–xxx

HOSTED BY

ELSEVIER

Contents lists available at ScienceDirect

Progress in Natural Science: Materials International

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

Original Research

Enhancing thermoelectric performance of Cu-modified $Bi_{0.5}Sb_{1.5}Te_3$ by electroless plating and annealing

Zhongyue Huang[a], He Zhang[a], Kun Zheng[b], Xueting Dai[a], Yuan Yu[a], Hefa Cheng[a], Fangqiu Zu[a,*], Zhi-Gang Chen[c,d,*]

[a] School of Materials Science & Engineering, Hefei University of Technology, Hefei 230009, China
[b] Institute of Microstructure and Properties of Advanced Materials, Beijing University of Technology, Beijing 100124, China
[c] Centre for Future Materials, University of Southern Queensland, Springfield, QLD 4300, Australia
[d] Materials Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

ARTICLE INFO

Keywords:
$Bi_{0.5}Sb_{1.5}Te_3$
Thermoelectric materials
Electroless plating
Annealing
Average zT

ABSTRACT

With the capacity of energy conversion from heat to electricity directly, thermoelectric materials have been considered as an alternative solution to global energy crisis. In this work, Cu modified $Bi_{0.5}Sb_{1.5}Te_3$ (BST) composites are prepared by a facile electroless plating Cu method, spark plasma sintering, and annealing. The annealed 0.22wt.%Cu/BST has an enhanced peak Figure of Merit (zT) of ~ 0.71 at 573 K with high average zT of 0.65 in the wide temperature range between 300 and 573 K. Due to the significant increase of electrical conductivity and low lattice thermal conductivity, the annealed 0.22wt.%Cu/BST shifts peak zT to high temperature, and shows 492% enhancement than that of pristine BST with zT of 0.12 at 573 K. Through detailed structural characterization of the annealed 0.22wt.%Cu/BST, we found that Cu can dope into BST matrix and further form Cu_2Te nanoprecipitates, dislocations, and massive grain boundaries, leading to a low lattice thermal conductivity of 0.30 $Wm^{-1}K^{-1}$ in the annealed 0.22wt.%Cu/BST. Such enhanced peak zT in high-temperature and high average zT in the wide temperature range shows that the electroless plating Cu method and annealing can improve the thermoelectric performance of commercial BST and expand the applicability of Bi_2Te_3 thermoelectric materials in the power generations.

1. Introduction

Thermoelectric materials, directly converting waste heat to electrical energy without any emissions or vibrational parts, can be a candidate in global sustainable energy solution [1–5]. The performance of thermoelectric materials is characterized by the dimensionless Figure of Merit (zT), $zT = S^2\sigma T/\kappa$, where S, σ, κ and T denote the Seebeck coefficient, electrical conductivity, thermal conductivity (including electronic component κ_e and lattice component κ_l), and absolute temperature, respectively [6,7]. Accordingly, a good thermoelectric material should combine high S, σ, and low κ [8,9]. To obtain high zT value, extensive approaches, including band convergence [10], resonant state doping [11], energy filtering [12], and quantum confinement [13,14], has been used to increase $S^2\sigma$. Another way is to reduce κ_l without sacrificing the electric properties by adjusting point defects [15,16], and using nanotechnology [17–19].

As the best thermoelectric candidate near room temperature, $Bi_{0.5}Sb_{1.5}Te_3$ (BST) shows good zT value [20–24]. However, the narrow working temperature range of BST significantly restricts its large-scale applications in power generations [25]. Thus, how to enhance thermoelectric performance at relative wide temperature range and to obtain a high average zT is of critical significance. Previous studies show that, introducing interfaces, including grain boundaries and secondary phase, can reduce κ_l through phonon scattering to enhance thermoelectric performance of BST [25,26]. However, most of the traditional methods are high-cost and low-yield, which are not suitable for commercial production [18,27]. Electroless plating technique [25,28] is a metal deposition process by controlling the oxidation-reduction reaction under the catalysis of metal [29,30], which can effectively induce massive interfaces without tedious steps compared with sol-gel method and hydrothermal synthesis [18,31].

Extensive studies have shown that transition metal doping in Bi_2Te_3 (BT) can tune their electron and phonon transport properties [32–35]. Especially, transition metals, such as Fe [36–39], Cr [40–42], Mn [32,43–45], V [46], Sn [47], and Cu [33,48], have been widely substituted into bulk BT to tune the physical and chemical properties. As a

Peer review under responsibility of Chinese Materials Research Society.
* Corresponding authors.
E-mail addresses: fangqiuzu@hotmail.com (F. Zu), zhigang.chen@usq.edu.au (Z.-G. Chen).

https://doi.org/10.1016/j.pnsc.2018.02.007
Received 14 November 2017; Accepted 11 January 2018

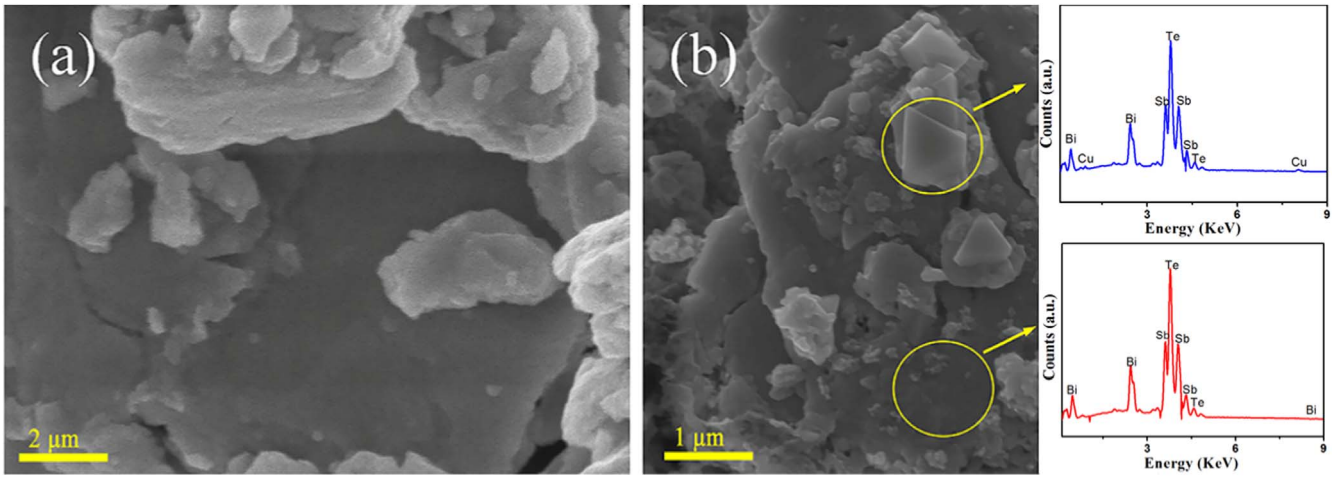

Fig. 1. FE-SEM images of (a) pristine BST powders; (b) 0.22wt.%Cu/BST powders with EDS profiles detected at the marked in b.

typical dopant candidate, Cu has been widely used in *p*-type BST, in which Cu dopant can enlarge bandgap of Cu-modified BST to improve $S^2\sigma$ and reduce κ_l via introducing point defects [16,49]. In this study, we choose Cu as an electroless plating element to enhance thermoelectric performance of the commercial BST. After detailed characterization and performance evaluations, we found that Cu can effectively tune σ and lower κ_l. Further annealing heat treatment, an enhanced peak zT shifts to high temperature range, and a high average zT is obtained.

2. Material and methods

Commercial BST powders with a grain size of 200 μm were chosen as the matrix. The BST powders first were washed by 5% HNO_3 solution at 20 ℃ through ultrasonic for 30 min and cleaned three times using deionized water for removing the impurities. After that, the powders were placed into plating solution consisting of copper sulphate (5 g L^{-1}), formaldehyde (7 ml L^{-1}) as the reducing agent, EDTA-2Na (20 g L^{-1}) as the complex agents, and sodium hydrate to adjust pH (pH = 8–9). The electroless plating powders were washed with deionized water, then dried at 333 K in an oven, finally reduced under hydrogen atmosphere at 573 K. The content of copper was determined by atomic absorption spectroscopy (AA800, Perkin Elmei).

The BST and 0.22wt.%Cu/BST powders were annealed at 623 K for 2 h under argon atmosphere, respectively. The powders were sintered by spark plasma sintering under a pressure of 40 MPa at 673 K for 5 min. For convenience, these samples were named pristine BST, annealed BST, 0.22wt.%Cu/BST and annealed 0.22wt.%Cu/BST, respectively.

The crystal structures of as-synthesized products and sintered pellets were characterized by X-ray diffraction (XRD) (D/MAX2500V, Rigaku) at room temperature, recorded on an X-ray diffractometer equipped with graphite monochromatized, Cu Kα radiation (λ = 1.5406 Å). The morphological, structural, and chemical characteristics of as-synthesized products and sintered pellets were observed by field-emission scanning electron microscopy (FE-SEM) (SU8020, Hitachi), field-emission scanning electron microscopy (EVO18, ZEISS, Germany) and transmission electron microscopy (TEM, FEI F20). The rough distribution and concentration of elements were tested by mapping a large area (1.14 mm × 0.88 mm). The grain boundaries in 0.22wt.%Cu/BST were revealed by backscatter electron image (BSE) and the composition is determined by energy dispersive spectrometer (EDS). The bonding behaviour of the samples was determined by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo).

The Hall coefficient was measured by physical property measurement system (PPMS) at room temperature. The bulk samples were cut into rectangular bars (3 mm × 3 mm × 16 mm) for, σ and S measurements under inert-gas atmosphere at temperatures ranging from room temperature to 623 K via commercial LSR-3 (Linseis) equipment. κ was calculated using $\kappa = DC_p\rho$, where D is the thermal diffusivity, specific heat (Cp) and thermal diffusivity (λ) of samples were measured by DSC (Diamond DSC 8500, PerkinElmer, US), and laser flash apparatus (LFA457, NETZSCH, Germany). Densities (ρ) of bulks were measured by using Archimedes' method. κ was calculated by the equation $\kappa = \rho C_p \lambda$.

3. Results and discussion

Fig. 1(a) and (b) show the typical secondary-electron SEM images of the pristine BST and 0.22wt.%Cu/BST powders. As can be seen, pristine BST powders have relatively smooth surfaces. In contrast, a few flakes with sizes in the range from 500 nm to 1 μm (Fig. 1(b)) are individually located on the surface of the matrix BST powders. Such flakes can be confirmed as containing Cu precipitates from EDS analysis. These containing Cu flakes can aggregate at grain boundaries after SPS sintering, which could provide an additional electrical path for the carriers as comparing with pristine BST.

To identify the crystal structures of the products, XRD was employed and the results are shown in Fig. 2(a). From which, rhombohedral $Bi_{0.5}Sb_{1.5}Te_3$ phase (PDF #49-1713) can be indexed for all samples. A few peaks from Cu_2Te (PDF #39-1061) can be indexed for the Cu/BST samples, indicating that containing Cu precipitates has reacted with Te to form Cu_2Te. To further verify the valence state of Cu in the products, XPS was used to analyse the copper ion of the 0.22wt.%Cu/BST and annealed 0.22wt.%Cu/BST and the results are shown in Fig. 2(b). As can be seen, the peak of $Cu_2p_{3/2}$ locates at 932.4 eV and no satellite peak can be observed, suggesting Cu has one state. Generally, Cu exists as metallic with univalence state. To illustrate the composition of the samples, we performed the back-scattering SEM image and corresponding EDS profiles of the annealed 0.22wt.%Cu/BST and the results are shown in Fig. 2(c). After the quantitate analysis of these two typical profiles, we found that the Te content of Spectrum 2 is much higher than that of Spectrum 1, suggesting that partial Te has diffused and alloyed with Cu to form Cu_2Te nanoprecipitates, which will be