Studies on surface preparation and smoothness of nanostructured Bi$_2$Te$_3$-based alloys by electrochemical and mechanical methods

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ABSTRACT

Significant improvements in the dimensionless thermoelectric figure-of-merit (ZT) for nanostructured bismuth telluride, Bi$_2$Te$_3$, and its alloys have been demonstrated. In designing high-performance thermoelectric devices, variations in the thermal and electrical contact resistances due to interfacial effects between the nanostructured alloy and the metallic electrodes remain a significant issue. Smooth scratch-free surfaces should provide a baseline for contact resistance studies. In this paper, the root mean square roughness over a 10 $\mu$m$^2$ of nanostructured bismuth tellurium based alloys was reduced from 133 nm to 1.9 nm by a procedure consisting of electrolysis, mechanical polishing, and chemical mechanical polishing (CMP). Post-CMP cleaning was also developed to yield a wettable surface for the subsequent conformable metallization.

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1. Introduction

Nanostructured thermoelectric alloys exhibiting an enhanced dimensionless thermoelectric figure-of-merit (ZT) have attracted considerable interest recently for use in high-performance thermoelectric devices [1–3]. In particular, nanostructured p-type bismuth antimony tellurides have achieved a peak ZT of about 1.4 at 100 °C [1]. Bi$_2$Te$_3$-based alloys (Bi$_x$Sb$_{2-x}$Te$_3$ as the p-type and Bi$_2$Se$_y$Te$_{3-y}$ as the n-type) are the most widely used thermoelectric materials near room temperature. Device performance not only depends on ZT, but also on the electrical and thermal contact resistances between the electrodes and the thermoelectric materials [4,5]. Interfacial electrical and thermal contact resistances depend on the interface morphology. Surface roughness is an important parameter to control the interface morphology. One limit of the interface control is to achieve smooth and scratch-free surfaces. However, very little research has been conducted in the surface treatment of Bi$_2$Te$_3$-based alloys, especially nanostructured thermoelectric materials [6]. In conventional polishing processes, scratches are inevitably generated on the surface because of the relatively low hardness of Bi$_2$Te$_3$-based alloys compared with abrasives such as alumina or silica. In addition, nanostructured alloys have many grain boundaries which are weak points for mechanical or chemical treatment.

This article presents a technique to prepare smooth scratch-free surfaces of nanostructured Bi$_2$Te$_3$-based alloys by electrolysis, mechanical polishing, and chemical mechanical polishing (CMP). A post-CMP method was also developed to achieve a wettable surface for the subsequent metallization. Root mean square (RMS) surface roughness of 1.9 nm is achieved. Such smooth surfaces will be of fundamental interest for studying interfacial electrical and thermal contact resistances, and is particularly convenient for interfacial thermal resistance measurements using time-domain thermoreflectance (TDTF) technique [7–9].

2. Experimental

2.1. Sample fabrication

Bulk nanostructured Bi$_2$Te$_3$-based materials, p-type (alloyed with Sb as Bi$_x$Sb$_{2-x}$Te$_3$) and n-type (alloyed with Se as Bi$_2$Se$_y$Te$_{3-y}$) disk samples of 25 mm in diameter and 2 mm in thickness were made by a ball milling and hot pressing method [1]. After hot pressing, both sides of the disk sample were polished using sand paper. This initial surface was used as a reference for the polishing process. A South Bay Technologies Model 920 polishing tool was used for all polishing processes.

2.2. Measurements

A Nanoscope IIIa atomic force microscope (AFM) was used to scan the surfaces and calculate the root mean square (RMS) rough-
ness. A KLA-Tencor P16 profilometer was used to do line-scan across the surface for dissolution rate evaluation. Contact angle was measured by a static contact angle goniometer, Kyowa Kaimen CA-X. Electrochemical measurement, including cyclic voltammogram, open circuit potential, static potentiodynamic polarization was performed using a Gamry PC14/300 potentiostat/galvanostat system. A platinum mesh was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode in standard three-electrode system. The experiments were successively carried out on n-type nanostructured Bi$_2$Se$_{y}$Te$_{3-y}$ alloys at first and then on p-type Bi$_x$Sb$_2$–xTe$_3$.

3. Results and discussion

Fig. 1(a) is an AFM image of the initial surface and exhibits a root mean square roughness of 133 nm. At this roughness, mechanical polishing will require a long processing time to reach a low surface roughness. However, polishing for an extended period of time has a high possibility of generating deep scratches or chemical corrosion, particularly in nanostructured alloys which are prone to such issues due to the abundant grain boundaries. The details of Figs. 1(b)–(d) are described in the subsequent sections.

A previous paper reported that mixtures of NaOH–tartaric acid form a good electrolyte for electrolytic etching of Bi$_2$Te$_3$ with the goal of achieving a preliminary flat surface to reduce processing time for the following polishing steps [6]. However, very few papers provided detailed explanation of this method. Here, we tried to understand and utilize this method from an electrochemical perspective. We were interested in the range of pH and potentials where it is possible to dissolve both major species of bismuth and tellurium in an aqueous solution. According to the Pourbaix diagram of Bi$_2$Te$_3$, tellurium is soluble as TeO$_4^{2-}$ but bismuth precipitates as insoluble Bi$_2$O$_3$ in a range at pH > 7.5 [10,11]. If applying potentials larger than 1.5 V at pH > 10.5, tellurium is still soluble as TeO$_4^{2-}$ and bismuth would form Bi$_2$O$_5$. Based on reactions relating aqueous bismuth and tellurium species and its precipitates, Bi$_2$O$_5$ would react with hydrogen cations to become Bi$^{3+}$ which would dissolve into solution [11,12].

Fig. 2 is the anodic wave of cyclic voltammetry in a 10% sodium hydroxide solution and a mixture of 10% sodium hydroxide and 5% tartaric acid.
tartaric acid to make pH 11.5 solutions. The rise in current density is less pronounced when tartaric acid is not used. It leads us to believe that tartaric acid performs the role of providing hydrogen cations for Bi₂O₅ in the electrolysis reaction. In principle, an ideal electrolysis process can achieve a low surface roughness by itself, but at the cost of greater surface damage due to a longer processing time. SEM pictures of surfaces after electrolyzing at 1.5 V for 30 s and 1.5 V for 60 s are shown in Fig. 3. These figures confirm that electrolysis at longer processing time damages the surface, with cracks forming at the grain boundaries. Thus, the initial surface was electrolyzed at 1.5 V for 30 s in a mixture of 10% NaOH and 5% tartaric acid to achieve a preliminary flat surface. The RMS roughness was reduced from 133 nm to 52 nm, as seen in Fig. 1(b).

The samples were then mechanically polished on a Buehler Trident cloth pad with an upper soft cloth surface and lower hard polyurethane support. A composite polishing pad is important for nanostructured Bi₂Te₃-based alloys because the upper soft cloth will prevent deep scratches while the lower hard supporting pad will prevent the surface from being polished along its beginning topography. The slurry used here is a 5 wt% 0.05 μm colloidal silica at pH of 5 adjusted by nitric acid, which is a good etchant for Bi₂Se₂Te₃−y alloys, was added to adjust the pH. Fig. 4(a) shows the open circuit potential (OCP) of n-type nanostructured Bi₂Se₂Te₃−y alloys as a function of the pH value. At pH values ranging from 3.5 to 9, bismuth forms insoluble Bi₂O₃. At a pH of 5, OCP decreased to a stable value indicating the formation of passivation layer. At a pH of 3.5, OCP decreased first and then increased. The reason could be that TeO₃ is not stable at low pH acidic solution and would be reduced to TeO₂ or HTeO₂⁺ based on thermodynamic expressions of the Bi₂Te₃ system [10,12]. For general conditions, it would form HTeO₂⁺ dissolved in slurry to increase OCP. Therefore, the pH needs to be controlled between 4 and 7 to prevent Te dissolution. So, the slurry pH we used here was 5. In general, hydrogen peroxide (H₂O₂) can be utilized in polishing slurries as an oxidizer to enhance the passivating reaction and some inhibitors, such as benzotriazole (BTA), are also added to avoid isotropic etching. Fig. 4(b) is the polarization scans with and without H₂O₂ and BTA. At a pH of 5, there is a sign of passivation at the anodic current branch. The film may not completely passivate the surface but may still decrease the dissolution rate, as is expected according to the results for open circuit potential. In the presence of 1 vol% hydrogen peroxide, the corrosion potential increased and the corrosion current density decreased. This result reveals that the effect of adding an extra oxidizer would decrease the corrosion rate. We tried to add more hydrogen peroxide up to 5 vol% into the system, but the corrosion potential and current did not show any significant change. The reason could be that the surface is already in its passive state above 1 vol% H₂O₂ and that etching is likely controlled by ionic diffusion through a passivation layer [13].

In an efficient CMP operation, the dissolution rate at a recessed region on the uneven surface should be as small as possible to avoid isotropic etching. Benzotriazole (BTA) is a well-known corrosion inhibitor for copper, copper–alloys, and other metal surfaces [14]. The effect of BTA on metal CMP to reduce the corrosion in the recessed areas has also been studied [15]. If a 0.1 vol% BTA is added into 1 vol% H₂O₂ pH 5 slurry, the potential drop became more positive and the corrosion current density decreased, and there was pronounced passivation sign between 0 V and 0.8 V SCE (saturated calomel electrode), as shown in Fig. 4(b). Fig. 4(c) shows an average dissolution rate to provide evidence that a protective layer was formed using both 1% hydrogen peroxide and 0.1% benzotriazole in slurry. Based on previous studies [14–17], even a small amount of BTA reduces the dissolution rate significantly and further increase of BTA concentration does not enhance the metal protection. As mentioned above, CMP slurry for the nanostructured Bi₂Se₂Te₃−y alloys is 1% hydrogen peroxide, 0.1% benzotriazole, and 5 wt% 0.05 μm colloidal silica at pH of 5 adjusted by nitric acid.
Fig. 4. (a) Variation of OCP with time in the slurry in different pHs, (b) polarization curves for adding H₂O₂ and BTA in pH slurry, and (c) effect of H₂O₂ and BTA on the dissolution rate in pH 5 slurry.

acid. Fig. 1(d) shows a scratch-free surface after 5 min of chemical mechanical polishing. As a result, a scratch-free surface with 1.9 nm RMS roughness over 10 μm² was achieved on nanostructured Bi₂Se₃₋ₓTeₓ alloys by 30 s electrolysis, 30 min mechanical polishing, and 5 min chemical mechanical polishing.

Since the CMP process leaves abrasive particles, trace metal, and organic component on the surface, post-CMP cleaning is necessary. Any particles left behind has a significant effect in creating imperfections ranging from bumps or pits to regions of excessive contact resistance or to causes non-uniform thin metal transducer layer for pump-and-probe measurement [18,19]. On the other hand, almost the entire surface of Bi₂Se₃₋ₓTeₓ alloys would be covered with a hydrophobic thin oxide layer after CMP, which functions poorly as nucleation site for metallization because the growth of metal film on substrates is classified by the same principles as wetting or nonwetting of liquids [20,21]. If the film wets the substrate, the atoms are more strongly bound to the substrate than to each other and grow layer-by-layer (Frank–van der Merwe growth). In contrast, if the film wets poorly, the atoms are more strongly bound to each other than to the substrate and grow three-dimensional islands (Volmer–Weber growth). Volmer–Weber growth is similar to liquid droplets with a large contact angle and is usually not desirable for technological applications. Therefore, post-CMP cleaning must yield a wettable and clean surface beneficial to subsequent metallization processes. The contact angle was used to evaluate wettability and particle removal efficiency [18,22]. Generally, the number of residual slurry particles decreases with decreasing contact angle in the region until reaching a threshold in wettability [22]. A 0.5% bromine in ethanol solution was chosen to remove the thin oxide on Bi₂Te₃-based alloys [6]. After bromine–ethanol treatment, a 5% additive (product name: CLEAN-100, Wako Pure Chemical Industries Ltd.) was chosen to improve the wettability, dissolve the organic components, and promote lift-off of particles from the substrate [19].

After 1 min of immersing in bromine-ethanol at room temperature and a 5 min immersion in CLEAN-100 at 45 °C with sonication, the contact angle with the sample surface and water was measured, as shown in Fig. 5. The sample surface with and without post-CMP cleaning showed a contact angle of 53.6° and 79.7°, respectively. So, it is believable that a metal film would wet on the nanostructured Bi₂Se₃₋ₓTeₓ surface after cleaning. 100 nm nickel films by sputter-
ing on sample surfaces with and without post-CMP cleaning were evaluated by SEM observation (Fig. 6(a) and (c)). The SEM results are consistent with wettability of liquids where a conformable nickel film was formed on the wettable surface, and cracked on the non-wetting surface where metal islands can be clearly seen. AFM was also used to measure the roughness of the 100 nm nickel films sputtered on the surface of nanostructured Bi$_2$Se$_{1-x}$Te$_{3-y}$ alloys with and without post-CMP cleaning (Fig. 6(b) and (d)). Uniform nickel film can be achieved on wettable surface. Poor wettability has relatively large surface roughness because poor nucleation results in growing three-dimensional islands. These results support the SEM observation and can be explained by Volmer–Weber growth model.

These processes were also successfully reproduced on p-type Bi$_x$Sb$_{2-x}$Te$_3$ samples with the same performance. We performed this process sequence on several samples of both n- and p-types to prove that the smooth scratch-free surface can be achieved on nanostructured Bi$_2$Te$_3$-based alloys. Based on this work, more experiments and investigations can be carried out for a complete understanding of the interfacial effect on mechanical strength and contact resistance of nanostructured Bi$_2$Te$_3$-based alloys.

4. Conclusions

In this paper, a new polishing process involving electrolysis, mechanical polishing, chemical mechanical polishing, and post-CMP cleaning was developed to fabricate scratch-free surfaces with a 1.9 nm root mean square roughness over a 10 $\mu$m$^2$ on both n- and p-type nanostructured Bi$_2$Te$_3$-based alloys. It was found that an optimal electrolysis treatment can preliminarily reduce surface roughness in a short time. Mechanical polishing, using a composite pad and slurry of 5 wt% 0.05 $\mu$m alumina, was then conducted to achieve global planarization. Chemical mechanical polishing was then used to remove scratches by softening the surface. The slurry used in this process consisted of 1% hydrogen peroxide, 0.1% benzotriazole, and 5 wt% 0.05 $\mu$m colloidal silica at pH of 5. To achieve a wettable surface for subsequent metallization, a 0.5% bromine in ethanol solution with 5% WAKO CLEAN-100 additive was used for post-CMP cleaning. Conformable metallization by sputtering was then achieved on the wettable and smooth surface.

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Appendix A. Supplementary data


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