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Improved thermoelectric performance of a film device induced by densely columnar Cu electrode

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ABSTRACT

In this study, it was found that the columnar Cu film is similar as a parallel microchannel which can create some sort of channels for the easy transport of electrons and phonons in the device. The *p*-$Bi_{0.5}Sb_{1.5}Te_3$, *n*-$Bi_2Se_{0.3}Te_{2.7}$ and Cu films were fabricated by a magnetron sputtering method. These films have been integrated into low-dimension cross-plane devices using mask-assisted deposition technology. The performance of the micro-device with densely columnar Cu film electrode has been tested, which was very superior to that of the device with ordinary structure electrode. For the typical device with 98 pairs of *p*/*n* couples, the output voltage and maximum power were up to 120.5 mV and 145.2 μW, respectively, for a temperature difference of 4 K. The device could produce a 14.6 K maximum temperature difference at current of 160 mA. The response time to reach the steady condition was less than 2 S. The results prove that excellent performance of micro-device can be realized by integrating the densely columnar Cu electrode.

1. Introduction

Solid-state thermoelectric (TE) micro-devices have been frequently studied in recent [1–4]. Unfortunately, many non-idealities become apparent and must be considered when moving from bulk to thin-film devices. Whereas electrical and thermal contact resistance and heat generation in the current carrying connections all become critical for thin-film devices [5]. For practically achievable values of modern Bi_2Te_3 heat exchangers, the impact of modern parasitic resistances results in a 50% reduction in the figure of merit at length scales less than ~0.5 μm [6]. Some of the highest performing thin-film TE materials with material *ZT* values in excess of 2 only achieve device performance equivalent to a material *ZT* of less than 0.4 when all the passive losses inherent to the device design are taken into account [7,8], i.e. an effective device $ZT < 0.4$. Joule heating at the metal-semiconductor interface has been a primary component in the reduction of theoretical cooling predictions by as much as 97% [5,9]. The contact resistance for thin-film device is a bottleneck, which badly confines the performance of TE micro-devices. To overcome this issue, numerous research efforts to explore various electrodes for devices have been done [10–14]. These reported methods have some other advantages, for example, excellent electrical conductivity and multilayered structure design for electrodes, but with the drawback of poor electrical and thermal conductivity at the metal-semiconductor interfaces. However, the columnar structuring process possibly induces a favorable change in the Fermi surface topology to improve the problem. Besides, the columnar structure electrode is similar as a parallel microchannel which can create some sort of channels for the easy transport of electrons and phonons in the device.

Among the metal electrodes, Cu is an attractive material, one of the cheapest common metals and an environment friendly product. To improve the properties of Cu as electrode materials for TE micro-devices, an efficient way is to control the structure of Cu nanomaterials by a simple magnetron sputtering method. Using densely columnar film as electrode is one of the most effective approaches to enhance micro-devices performance. Here, it is found that densely columnar Cu film is introduced into a cross-plane device as electrode (reducing Joule heating and improving thermal transport) using magnetron sputtering, which can greatly improve electrical and thermal transport and dramatically enhance performance of a vertical-type micro-device with Bi_2T_3-based thin-film couples. It is also the main emphasis on correlating device performance with electrode structure. Such correlation provides valuable information for the construction of various TE devices and

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provides guidance for thermal management applications requiring simultaneous control over electrical and thermal conductivities.

2. Experimental section

In this work, *p*-$Bi_{0.5}Sb_{1.5}Te_3$ and *n*-$Bi_2Se_{0.3}Te_{2.7}$ films were grown at 300 °C deposition temperature and 2 Pa working pressure in a magnetron sputtering system. Commercial 60-mm-diameter hot-pressed $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Se_{0.3}Te_{2.7}$ and Te (99.99% purity) targets (Purchased from General Research Institute for Nonferrous Metals, China) were used for co-sputtering to compensate for evaporated tellurium at high temperature. The target direct-current powers were set to 35 W and 40 W for $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Se_{0.3}Te_{2.7}$, respectively. While the Te target was connected to a radiofrequency power supply with power of 30 W. Cu target (99.99% purity) was sputtered by target power of 25 W for the columnar or the ordinary Cu films at 300 °C deposition temperature and 2 Pa or 1 Pa working pressure, respectively. The base pressure was lower than 2×10^{-4} Pa. Before deposition, AlN substrates were cleaned thoroughly by diluted nitric acid and acetone, and dried under the nitrogen airflow.

The stainless steel masks with designed patterns were used to fabricate device connected electrically in series, and the masks include mask for TE film ($mask_f$) and masks for electrodes ($mask_e$), respectively. Connection metal pads of Cu were first deposited on the lower and the upper AlN plates with thickness of 0.25 mm using magnetron sputtering and $mask_e$-assisted deposition technology, respectively. The size of lower (upper) AlN plate is 35 (30) mm × 30 mm. Then *p*-$Bi_{0.5}Sb_{1.5}Te_3$ and *n*-$Bi_2Se_{0.3}Te_{2.7}$ film couples with 1 mm × 1 mm in area were deposited onto metal pads under $mask_f$, respectively. Finally, the lower AlN plate with 98 *p*-type elements and the upper AlN plate with 98 *n*-type elements were bonded using flip-chip bonding techniques to form a 98 pairs of *p*/*n* couples module. The thickness of TE films is about 2 μm and the Cu electrode thickness is about 500 nm by controlling deposition rate and sputtering time. Before operation, the devices were annealed in N_2 gas at 150 °C for 0.5 h. Annealing improved the mechanical and electrical contacts between the thermoelectric elements and interconnects, and also improved the thermoelectric figure-of-merit of the thermoelectric materials.

The crystal structures of $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Se_{0.3}Te_{2.7}$ films grown on SiO_2 substrates were examined by X-ray diffraction (XRD, Rigaku D/MAX 2200) using Cu K_α radiation ($\lambda = 0.154056$ nm). The films and couples morphology were observed by field-emission scanning electron microscopy (FE-SEM, Sirion 200). The compositions were detected by energy dispersive X-ray spectroscopy (EDX). Surface profilometry (Ambios XP-2, USA) was used to measure the film thickness. The electrical conductivity (σ) and Seebeck coefficient (S) were simultaneously measured on thin films deposited on $5 \times 15 \times 1$ mm^3 substrates using a ZEM-3 (Ulvac Riko, Inc.). The thermal conductivity (κ) data were collected using a Laser PIT (Ulvac Riko, Inc.) at room temperature. The principle of the measurement method is described in detail in Ref. [15]. The carrier concentration and mobility were determined using a four-probe measurement based on the Hall effects (ECOPIA HMS-3000) at room temperature. We also measured the overall resistance of the TE devices by a voltammetry method. The output voltages of the devices were measured by a DC digital voltage/current meter (Shanghai SB-2238) while applying a temperature difference between the hot and cold sides of the devices.

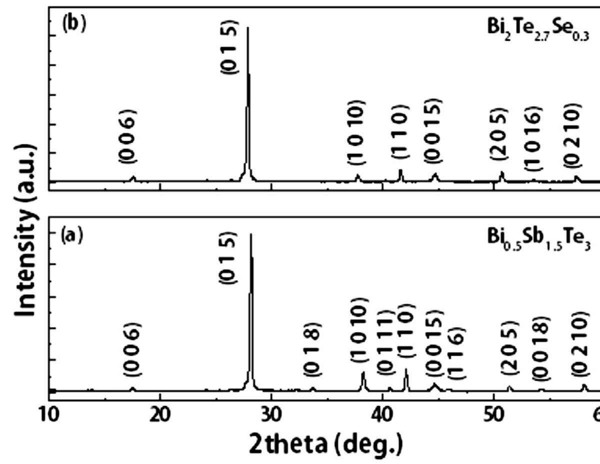

Fig. 1. XRD patterns of (a) $Bi_{0.5}Sb_{1.5}Te_3$ and (b) $Bi_2Se_{0.3}Te_{2.7}$ films.

3. Results and discussion

The *p*-$Bi_{0.5}Sb_{1.5}Te_3$ and *n*-$Bi_2Se_{0.3}Te_{2.7}$ films have been synthesized by a simple magnetron sputtering technique at 300 °C deposition temperature and 2 Pa working pressure. XRD patterns of $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Se_{0.3}Te_{2.7}$ films are shown in Fig. 1. For the both films, all peaks are indexed as rhombohedral phase (JCPDS 49-1713 and 50-0954 corresponding to Fig. 1a and b), implying the formation of polycrystalline structure. The intense and sharp XRD peaks from the films are typical signatures of a high degree of crystallinity. It reveals a single-phase product with slightly broadened reflections, which is typical for crystals with low dimensions.

The columnar and the ordinary Cu films are shown in Fig. 2. Seen from cross-sectional view (Fig. 2a), the columnar film is relatively dense and uniform, and a number of columns are existed in the film. As shown in Fig. 2a, we can observe that a large number of Cu columns are densely grown perpendicular to the substrate. In the film, the diameters of columns are in the range of 40–100 nm. The Cu columns array is similar as a parallel micro channel. By

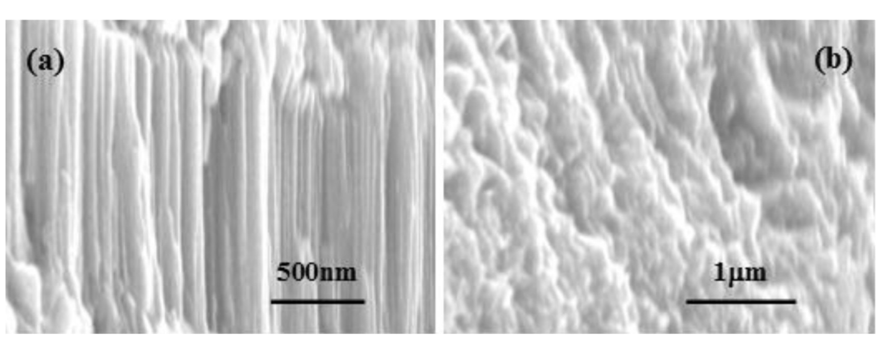

Fig. 2. SEM images of (a) columnar and (b) ordinary Cu films with cross-sectional view.

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