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Fabrication of Microstructured thermoelectric Bi_2Te_3 thin films by seed layer assisted electrodeposition

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ABSTRACT

In this work, bismuth telluride (Bi_2Te_3) thin films have been fabricated on Bi_2Te_3/ITO substrates by constant potential electrochemical deposition at room temperature. Bi_2Te_3 seed layers with different thicknesses (2 nm, 4 nm and 6 nm) were deposited onto ITO substrates using molecular beam epitaxy (MBE) method. The SEM images show that the morphology of Bi_2Te_3 thin films can be controlled not only by the deposition potential, but also the thickness of seed layer. Moreover, the morphologies of Bi_2Te_3 thin films with different thickness of seed layers tend to be similar and contain two-layer structure along the vertical direction after prolonged deposition time. Due to the two layers structure, Bi_2Te_3 thin films have shown different electrical conductivity performances. At room temperature, Bi_2Te_3 thin films with 4 nm-thick seed layer possess the maximum electrical conductivity value of 617.9 s cm^{-1}.

1. Introduction

Thermoelectric (TE) devices can convert wasted heat into electrical energy directly, showing great potential to relieve the crisis of energy depletion and global warming. TE device is a kind of solid state power generator that possesses many advantages such as exemption from moving part, excellent stability, long operating lifetime and it is easy to maintenance [1]. Figure of merit, a dimensionless quantity, is commonly used to characterize the thermoelectric performance of TE materials, which is defined as $ZT = S^2\sigma T/\kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, T is the absolute temperature and κ is the thermal conductivity, respectively [2]. In the last few decades, tremendous efforts have been made to search for TE materials with better performance [3]. The theoretical study indicates that the ZT in TE nanomaterials could be significantly enhanced due to the quantum confinement effect and phonon blocking effect [4, 5]. Therefore, there are two major ways to enhance thermoelectric performance: (1) suppressing the thermal conductivity without hampering the electric properties by increasing the interface scattering in virtue of phonon blocking effect; (2) enhancing the power factor based on the quantum confinement effect. As the conventional commercial TE materials, Bismuth telluride (Bi_2Te_3) and their alloys exhibit a good thermoelectric performance at room temperature. However, the current performances of Bi_2Te_3 are still far from satisfying the need of large-scale utilization. But the thin film technology is a potential method for the optimization of performances of Bi_2Te_3 [6].

To date, various fabrication methods such as sputtering [7, 8], evaporation [9, 10], electrochemical deposition [11] and metal organic chemical vapor deposition (MOCVD) [12] have been developed for Bi_2Te_3 films. Among these methods, electrochemical deposition has many advantages including easy scalability, simple equipment, high deposition rates and room temperature operation [13]. Seed layer assisted electrodeposition is a kind of emerging technology to prepare Bi_2Te_3 thin film with better-performance. According to the work of Li et al. [14], an Au-sputtered Al substrate was used to deposit Bi_2Te_3 film. And metal (i.e., nickel (Ni), cobalt (Co) and iron (Fe)) can also be used as sacrificial materials, referred to the work of Chang et al. [15]. Those works investigated the effects of metal seed layer during the electrochemical deposition process. In contrast, some researchers chose to sputter a layer of Bi_2Te_3 on its substrate and then electrochemically deposited Bi_2Te_3 thin films like Yoo et al. [16] and Cao. et al. [17]. As seed layers, Bi_2Te_3 thin films indeed affect the structure and performance according to results. In addition, lattice mismatch between deposited

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materials and substrates can be minimized [18]. The relationships between the microstructure and properties have been investigated [19], in which the microstructure mainly refers to grain sizes and surface morphologies. However, little light has been shed on the influence of thickness of seed layer on the surface morphology and TE performance.

In this work, Bi_2Te_3 thin films with different thickness as seed layer on ITO have been synthesized and investigated to optimize thin film morphology and structure. The morphology, structure, chemical compositions, electrical transport and Seebeck coefficient of potentiostatically deposited Bi_2Te_3 thin films have been adequately and deeply analyzed and studied.

2. Experimental materials and method

Different thicknesses of Bi_2Te_3 (2 nm, 4 nm, 6 nm) were deposited on ITO substrate as the seed layer by MBE. During the deposition, the pressure of vacuum chamber was fixed at 10^{-6} Pa and the substrate was heated at 160 °C. The source fluxes were from high purity Bi (99.99%) and Te (99.99%). Prior to deposition, the ITO surface was ultrasonically cleaned in acetone and ethanol respectively, then rinsed with deionized water and dried under a flow of nitrogen.

Electrochemical deposition was performed in conventional three-electrode electrochemical cell structure, in which the ITO with different thickness of seeds layer as the working electrode, and a platinum mesh was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. Bi_2Te_3 thin films were electrochemically deposited from an aqueous nitric acid at room temperature without stirring. And the scan rate was set in 20 mV per second. The electrolyte containing 0.008 m Bi^{3+} and 0.01 m $HTeO_2^+$ was prepared by the dissolution of $Bi(NO_3)_3 \cdot 5H_2O$ and TeO_2 in 1 m nitric acid. Before experiment, the electrolyte solution was deaerated by blowing purified nitrogen gas through for 10 minutes. After experiment, the samples were removed from the electrolyte and rinsed with nitric acid solution, ethanol and distilled water before dried in the air [17].

The morphology of samples was characterized with scanning electron microscope (SEM, ULTRA55-36-69). Energy dispersive X-ray spectroscopy (EDS) was employed to analyze the chemical compositions. An X-ray diffraction (XRD, 3KW D/MAX2200 V PC) in conventional θ-2θ mode with Cu-Kα radiation was used to observe the crystal structure. The electrical transport and thermoelectric properties were measured by a home-made device [20].

3. Results and discussion

3.1. Study of seed layer

Bi_2Te_3 thin films as seed layer synthesized by MBE were characterized by atomic force microscopy (AFM) in a tapping mode. It is obviously that the roughness of Bi_2Te_3 surface decreases with the increase of the thickness of the seed layer, as shown in Fig. 1. In the presence of 2 nm seed layer, the surface morphology exhibits similar surface roughness compared with the original ITO substrate. Fig. 1 shows roughness and reduction peak potential as a function of the seed layer thickness. We suspect that in a 3 nm roughness of substrate, a molecular beam epitaxy deposition 6 nm thicknesses of thin film tend to be continuous. (referring to Supporting Information Figure S1). As a matter of fact, different surface roughness could result in different active electrochemical surface, which may affect the deposition potential in the electrodeposition process will be shown in cyclic voltammograms (CV).

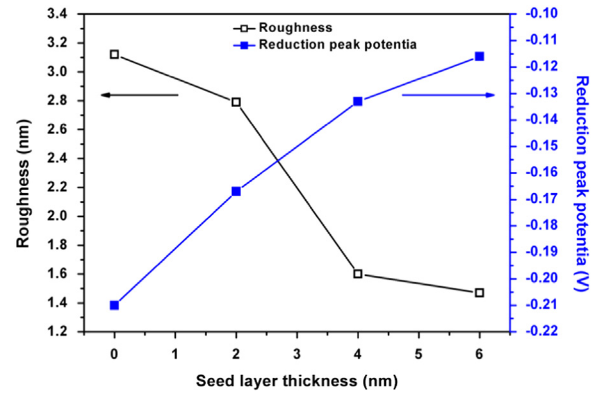

Fig. 1. Roughness and reduction peak potential as a function of the seed layer thickness.

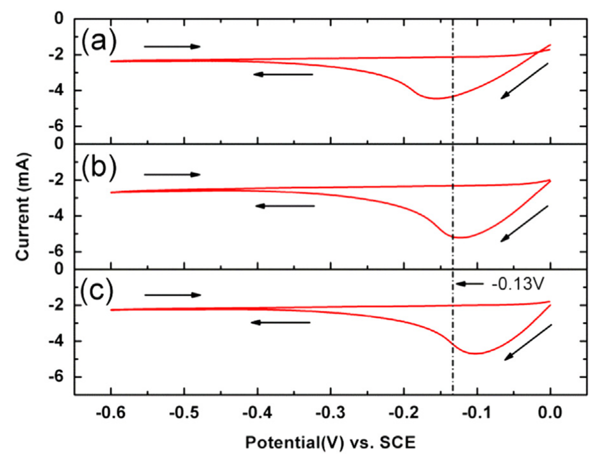

Fig. 2. Cyclic voltammograms of Bi_2Te_3 electrodeposition on ITO with different seed layer: (a) 2 nm; (b) 4 nm; and (c) 6 nm, respectively, in the solution containing 0.008 m Bi^{3+} and 0.01 m $HTeO_2^+$ in 1 m nitric acid at room temperature; scan rate was fixed at 20 mV s^{-1} while the SCE as reference electrode. The dotted line marked a potential at -0.13 V. Surface area = 0.9 cm^2.

CV were implemented in the electrolyte with the sweeping rate of 20 mV s^{-1} in these experiments, in which the ITO substrates with 2 nm, 4 nm and 6 nm Bi_2Te_3 seed layer were used as working electrode. As shown in Fig. 2, with the increasing thickness of seed layer, the cathode reduction potential shifts to high positive value. This phenomenon may due to the surface roughness effect [21]. The surface roughness decreases with the increases of seed layer thickness, and consequently, the active electrochemical surface decreases in the same manner. Then the cathode current decreases as well. In the presence of 2 nm seed layer, the substrate is incompletely covered with Bi_2Te_3 seed layer as shown in the AFM image (Figure S1 (a) and (b)), namely have a rougher surface. On the other aspect, the difference of surface roughness results in different electrical resistivity and then generates different electric fields between two electrodes. The different surface electrical resistivity of 4 nm and 6 nm seed layers leads to different reduction potentials. Namely, the rougher the surface, the greater the active electrochemical surface and the higher the energy required to restore. As for the 4 nm seed layer, it is almost coincided with cathode reduction peak (-0.13 V), but more negative than that of 6 nm seed layer and more positive than that of 2 nm seed layer. When the reduction potential appear at lower region [22, 23], the main reaction is the reduction of $HTeO_2^+$ as well as the Bi^{3+} to form the Bi_2Te_3, the overall reaction for the process is:

$$3HTeO_2^+ + 2Bi^{3+} + 18e^- + 9H^+ \rightarrow Bi_2Te_3 + 6H_2O$$