

Electrochemical Deposition of Nanocrystalline Bi-Te Films and Their Characterizations



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Abstract: Galvanostatic electrochemical processes were used to electrodeposit Bi-Te binary thin films. Single-phased Bi₂Te₃ and Bi₄Te₃ films were synthesized in turn on the same electrolyte. Bi₂Te₃ thin film was composed of regular nanorods with the length up to 100 nm and average width of 10 nm, which exhibits large specific areas and benefits to the application as thermoelectric (TE) materials. And the Bi₄Te₃ thin film is composed of nanoparticles which assemble greatly into irregular polyhedrons. The results prove that it is possible to tune the phase composition and morphology of Bi-Te binary thin films by changing the deposition parameters.

Key words: electrochemical deposition; galvanostatic; films; thermoelectric material; Bi₂Te₃; nanorods

Bismuth telluride (Bi₂Te₃) and its alloys are known as one of the best thermoelectric (TE) materials currently available near room temperature with their highest figure of merit $ZT \geq 1$, and most modern thermoelectric coolers, thermal sensors, and so on, are made from such materials^[1-3]. As is known that $ZT = (\alpha^2 \sigma / \kappa) T$, in which α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. Therefore, excellent TE materials require a perfect combination of high power factor ($\alpha^2 \sigma$) and low thermal conductivity κ ^[4]. Nanostructured materials and composites offer the potential advantage that overall material properties may be tailored by tuning the characterization size and/or composite structures. It is suggested that such a new generation of “complex” materials might exhibit enhanced thermoelectric properties^[5-7]. So nanostructured Bi₂Te₃ or its alloys may have better thermoelectric properties than the common bulk ones.

A traditional preparation method of Bi₂Te₃ is to melt the metal elements together^[8]. But this process requires an elevated temperature and a special protection against

oxidation, and the products are always coarse-grained, which is adverse to the decrease of thermal conductivity. Mechanical alloying (MA) is another effective technique to process bismuth telluride based alloys^[9,10]. But it needs a long duration and has strict requirement on raw materials. Besides, a powder metallurgy process and an evaporation method are effective techniques for the preparation of bismuth telluride (Bi₂Te₃) and its derivative compounds. However, these techniques do not lend themselves to the production of large-area thermoelectric elements. Electrochemical deposition^[11,12] may provide an alternative process to these classical methods. Furthermore, thin films can be directly obtained with electrodeposition techniques, which are useful for preparing thin-film elements, such as sensors.

Several researches on Bi-Te alloys electrodeposition have been reported. Takahashi et al^[13] have gained Bi-Te alloy films through electrochemical deposition, but the product contains not only Bi₂Te₃, but also BiTe and Te. Magri et al^[14] have acquired single-phased Bi₂Te₃ films via a similar process, but the grains are within micron-grade, not fine enough to exhibit the advantage of reducing the

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thermal conductivity. Sapp et al.^[15] have obtained nanowires of bismuth telluride with electrochemical deposition by applying a porous alumina template. Therefore, the size and shape of Bi-Te alloys are strictly limited by the alumina template.

In the present study, a galvanostatic process is used to electrodeposit Bi-Te films. Both the phase composition and morphology of Bi-Te nanostructures can be carefully controlled by tuning the deposition parameters without any other assistant devices. Based on the results of this study, it is possible to obtain single-phase Bi₂Te₃ thermoelectric thin films with large specific areas to achieve low thermal conductivity and to enhance the related thermoelectric properties.

1 Experiment

The deposition solution was prepared according to the published procedure^[14]. All chemicals were adopted without further purification. 15 mmol tellurium powder (99.999%) was dissolved into 1.0 mol/L nitric acid (500 mL, pH=0) at 80 °C in a fume hood. Vigorous stirring was continued until all the tellurium dissolved. Then 15 mmol Bi(NO₃)₃·5H₂O (A.R.) was added to the solution. The atomic ratio of Bi:Te was 1:1, and thus an exact or quasi Bi₂Te₃ could be expected according to Ref. [14].

Electrodeposition was carried out at a constant temperature of 25 °C. A traditional three-electrodes system was adopted for the electrochemical deposition of Bi-Te alloy films. The working electrode was a polished stainless-steel disk with the area of 15.14 cm² and thickness of 0.5 mm. A platinum sheet and an Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively.

Arbin BT-2000 Instrument was used for the galvanostatic deposition of Bi-Te alloy films. The current of 72 mA was used in the first 24 h working cycle. After this cycle, the working electrode was taken out carefully and another same electrode was put into the same solution, and the second working cycle of 24 h under the working current of 60 mA was carried out.

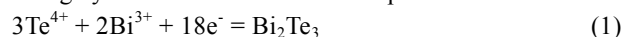
After the electrochemical deposition process, the two products were washed thoroughly in three steps in turn (0.1 mol/L nitric acid solution (pH=1), distilled water and absolute ethanol), followed by drying in air. Then the products were removed from the supports, and also ground into powders for phase composition and morphology characterization. Sample A and sample B were named for the first and the second products, respectively.

The phase composition of obtained samples were characterized with powder X-ray diffraction (XRD) patterns, using a Rigaku-D/MAX-2550PC X-ray diffractometer with Cu K α radiation ($\lambda=0.154056$ nm). The element analysis was taken on an EDAX PV-9900 energy dispersive

spectrometer (EDS) to make sure the component and element of products. Transmission electron microscopy (TEM) observation was taken on a JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV.

2 Results and Discussion

The XRD patterns of sample A and B are shown in Fig.1 and Fig.2, respectively. The pattern of sample A is in good agreement with Bi₂Te₃ phase with no other secondary phase. The lattice parameters are calculated as $a=0.4389$ nm and $c=3.0443$ nm, which are both very close to the reported values of $a=0.4395$ nm and $c=3.044$ nm from JCPDS# 82-0358. Therefore, it can be concluded that a single-phased Bi₂Te₃ compound is electrodeposited in the first working cycle. The reaction can be expressed as:



During this process, it can be observed that the initial deposit is in the color of pearl-gray, with compact surface. Then it becomes into dark-gray, even black with the deposition time increasing. Meanwhile, the surface also becomes looser and rougher with the thickness increasing. It can be attributed to the growth of dendrites which prevents the formation of a regular film when synthesizing thicker films. After removing the surface of the film, the interface that was in contact with the support electrode exhibits a uniform morphology with metallic luster.

The X-ray diffraction pattern in Fig.2 can be well indexed into Bi₄Te₃ phase. The cell constants of $a = 0.4450$ nm and $c = 4.1804$ nm are very close to the reported values of $a = 0.4451$ nm and $c = 4.189$ nm based on JCPDS# 75-1096, indicating that sample B is single-phased Bi₄Te₃. The energy dispersive spectroscopy (EDS) spectra of the two samples (Fig.3) reveals the only presence of Bi and Te peaks in the obtained powders. The spectra also exhibit that the ratio of Bi:Te in sample A is much higher than that of sample B. This is because in the first working cycle, the Bi³⁺ ions in the electrolyte are consumed more slowly than

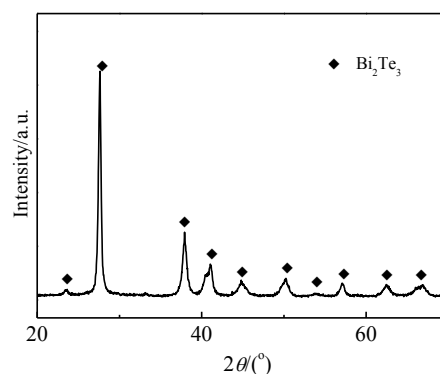


Fig.1 XRD pattern of sample A

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