Rare Metal Materials and Engineering
Volume 45, Issue 12, December 2016
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(12): 3108-3111.

ARTICLE

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 Bi_2Te_3 and Bi_4Te_3 films were synthesized in turn on the same electrolyte. Bi_2Te_3 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 Bi_4Te_3 thin film is composed of nanoparticles which assembl 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; Bi_2Te_3; nanorods

Bismuth telluride (Bi_2Te_3) 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 Bi_2Te_3 or its alloys may have better thermoelectric properties than the common bulk ones.

A traditional preparation method of Bi_2Te_3 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 (Bi_2Te_3) 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 Bi_2Te_3, but also BiTe and Te. Magri et al[14] have acquired single-phased Bi_2Te_3 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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Received date: March 7, 2016
Foundation item: National Natural Science Foundation of China (51201053); Zhejiang Province Xinmiao Talent (2013R407015)

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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 Bi_2Te_3 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 $Bi(NO_3)_3$ $5H_2O$ (A.R.) was added to the solution. The atomic ratio of Bi:Te was 1:1, and thus an exact or quasi Bi_2Te_3 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 cm^2 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 Kα radiation (λ=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 Bi_2Te_3 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 Bi_2Te_3 compound is electrodeposited in the first working cycle. The reaction can be expressed as:

$$3Te^{4+} + 2Bi^{3+} + 18e^{-} = Bi_2Te_3 \qquad (1)$$

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 Bi_4Te_3 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 Bi_4Te_3. 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 Bi^{3+} ions in the electrolyte are consumed more slowly than

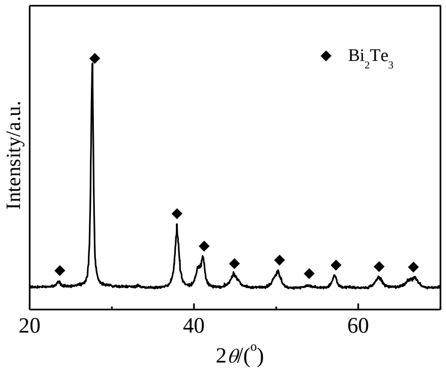

Fig.1 XRD pattern of sample A

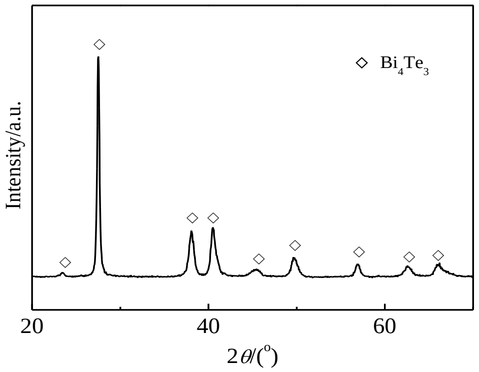

Fig.2 XRD pattern of sample B

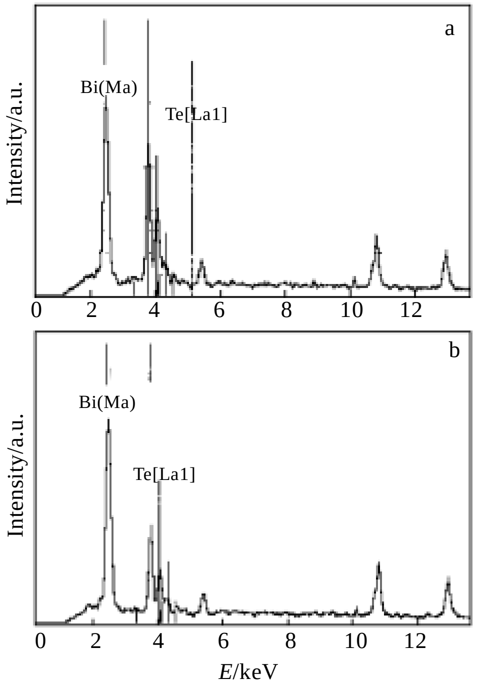

Fig.3 EDS spectra of sample A (a) and sample B (b)

$HTeO_2^+$ (telluryl ion) when forming Bi_2Te_3. Therefore, after the first cycle, Bi^{3+} ions in the solution are comparatively surplus to Bi_2Te_3 formation. Meanwhile, tellurium dioxide (TeO_2) precipitates from the solution in the form of white solid. Thus the content of $HTeO_2^+$ in the solution decreases furthermore. Therefore, Bi_4Te_3 comes into being in the second working cycle.

Scherrer Equation was also applied to calculate the average grain size of the samples. Scherrer Equation is as below:

$$L = K\lambda/\beta\cos\theta \qquad (2)$$

where, L is average grain size of powders, λ is wavelength of X-ray (in this study, $\lambda = 0.154\ 06$ nm), $\theta(^\circ)$ is Bragg angle of the diffraction peak, β(rad) is the Full-Width Half-Maximum (FWHM) value, and K is Scherrer Constant (here $K = 0.9$). Based on this equation, the average grain sizes of sample A and B are calculated depending on the three strong peaks. The average grain sizes of sample A and B are 15 nm and 18 nm, respectively, which indicates that the two samples are all fine-grained nanopowders with no obvious distinction in grain size.

The microstructures of sample A and sample B obtained by TEM observation are shown in Fig.4 and Fig.5, respectively. Fig.4a shows that sample A which is electrodeposited in the first 24 h consists of mainly nanorods. The particles scatter well, but a few clusters exist. Fig.4b confirms that sample A is regular nanorods with length up to 100 nm and average width of 10 nm. The particles of sample B is in the shape of irregular polyhedrons with the size from several hundreds nanometer to one micron, as shown in Fig.5. This is because all small

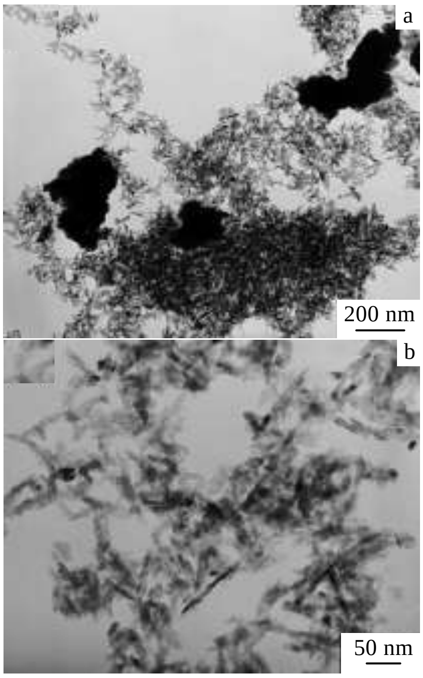

Fig.4 TEM images of sample A under high magnetization (a) and low magnetization (b)

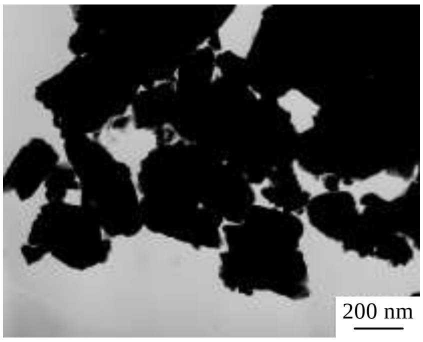

Fig.5 TEM image of sample B

particles assemble together into irregular clusters. Some nanoparticles can be observed from the edges of the polyhedrons in the shape of nanosphere. The appearance of clusters can be attributed to the high surface activity of nanoparticles. Considering that the depositing current density of sample A is higher than that of sample B, it implies that grains electrodeposited under a lower current density inclines to assemble, but this still need a further investigation.

3 Conclusions

1) Single-phased Bi_2Te_3 and Bi_4Te_3 films are synthesized in turn on the same electrolyte by galvanostatic electrochemical processes.

2) Bi_2Te_3 thin film is composed of regular nanorods with the length up to 100 nm and average width of 10 nm, which exhibits large specific areas and benefits the application as thermoelectric materials.

3) Bi_4Te_3 thin film is composed of nanoparticles which assemble greatly into irregular polyhedrons, and it may be attributed to a lower current density.

4) By carefully controlling the deposition parameters, it is possible to tune both the phase composition and morphology of obtained products as designed.

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电化学沉积制备纳米晶 Bi-Te 薄膜及其表征

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摘 要：采用恒电流电化学沉积工艺制备Bi-Te二元薄膜。随着沉积时间的变化，在同一个电极上依次出现了单相的Bi_2Te_3和Bi_4Te_3薄膜。其中，Bi_2Te_3薄膜是由规则的长度为100 nm左右，平均宽度为10 nm的纳米棒组成, 其具有非常大的比表面积，非常有利于其作为热电材料的应用。而Bi_4Te_3薄膜是由纳米颗粒团聚而成的不规则多面体组成。研究证明通过改变沉积参数，有可能在Bi-Te二元系统的沉积过程中对生成物的相组成和形貌进行调控。

关键词：电化学沉积；恒电流；薄膜；热电材料；Bi_2Te_3；纳米棒

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