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ScienceDirect
Ceramics International 38S (2012) S535–S538
CERAMICS INTERNATIONAL
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# Facile synthesis of thermoelectric films via spin-coating metastable precursors

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Available online 24 May 2011

**Abstract**

In this paper, we reported on a novel, simple, and cost-effective chemical route to fabrication of thermoelectric films, such as Bi, PbTe, and $Bi_2Te_3$. The films were prepared by spinning coating corresponding metastable precursor solutions, using $TeO_2$ and/or metallic salt as the starting materials, and $KBH_4$ as reductant. The phase structure and morphology of the films were characterized by X-ray diffraction and field-emission scanning electron microscopy, respectively. The formation mechanisms of the films were proposed. The electrical conductivity of the films was measured at room temperature.


*Keywords:* A. Films; C. Electrical conductivity; Spin-coating; Metastable precursor

## 1. Introduction

The performance of a thermoelectric (TE) material mainly depends on the dimensionless figure of merit $ZT$ ($ZT = \sigma S^2 T/\kappa$, where $T$ is the absolute temperature, $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the thermal conductivity of the material). However, it is a great challenge to obtain materials with high $ZT$ values as optimizing one parameter of $Z$ often adversely affects another. Theoretical calculations and experiments indicate that improvement in TE properties can be achieved as the dimensionality of materials is reduced [1–6]. Low dimensional materials such as films are of great interest for the construction of high performance TE devices.

TE thin films have been successfully prepared by several different methods, such as metal–organic chemical vapor deposition [4,7,8], molecular beam epitaxy [3,9], magnetron sputtering [10], pulsed laser deposition [11], hot-wall epitaxy [12], and electrodeposition [13–16]. Among these methods, electrodeposition is a simple and low-cost method. However, conductive substrates have to be used for electrodeposition. Compared with electrodeposition, chemical bath deposition is more facile, cost-effective and without special requirement for substrates. We recently reported PbTe films prepared by a chemical bath method from a metastable solution at room temperature [17]. Unfortunately, this method is unsuccessful to be extended to other TE films such as Bi, $Bi_2Te_3$, $Sb_2Te_3$. Recently, spin-coating technique has been widely used for manufacturing organic or oxide-based films. To our best knowledge, no work has been reported on fabrication of metal or intermetallic TE thin films via spin-coating processes. In this paper, we prepared Bi, PbTe, and $Bi_2Te_3$ thermoelectric films via spin-coating metastable precursor solutions.

## 2. Experimental

All reagents were analytical grade and directly used as received. Si(1 1 1) wafers were used as substrates after being cleaned sequentially with acetone, ethanol and deionized water. In a typical run for fabrication of Bi film, 1 mmol $Bi(NO_3)_3{\cdot}5H_2O$, 20 mmol KOH, 4 mmol sodium tartrate ($Na_2C_4H_4O_6$), and 8 mmol $KBH_4$ were dissolved in sequence in 50 ml deionized water. A colorless and transparent solution was formed. Then, the fresh precursor solution was spin-coated on Si(1 1 1) wafer with a rotation speed of 3000 rpm for several times and a film was generated on the substrate. The obtained film was rinsed in deionized water to remove the ions, such as $Na^+$, $K^+$ and $OH^-$ adsorbed on the surface of the film, and then dried in vacuum. The film is called as sample I.

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0272-8842/$36.00 
doi:10.1016/j.ceramint.2011.05.070

PbTe film was fabricated using the same procedure as that for Bi film but the precursor solution for PbTe film was prepared by dissolving 1 mmol $Pb(Ac)_2{\cdot}3H_2O$, 1 mmol $TeO_2$, 20 mmol KOH, and 16 mmol $KBH_4$ sequentially in 50 ml deionized water. The film prepared is called as sample II.

$Bi_2Te_3$ film was also prepared by this method using 100 ml precursor containing 2 mmol $Bi(NO_3)_3{\cdot}5H_2O$, 3 mmol $TeO_2$, 40 mmol KOH, 8 mmol $Na_2C_4H_4O_6$, and 16 mmol $KBH_4$. The films were annealed at 200 °C, 350 °C, and 500 °C for about 5 h under flowing argon and named as samples IIIA, IIIB, and IIIC, respectively.

The phase structure of the films was determined by X-ray diffraction (XRD, Bruker D8 Advanced) with Cu Kα radiation (λ = 1.5406Å) and the morphology of the films was observed by field emission scanning electron microscopy (FE-SEM, Quanta 200 FEG). The electrical conductivity of samples I, II, and IIIC was measured at room temperature by a four-probe method in van der Pauw configuration.

## 3. Results and discussion

The typical XRD patterns of samples I and II prepared at room temperature are shown in Fig. 1. The diffraction peaks except the peak for Si(1 1 1) in Fig. 1(a) and (b) can be indexed to the reported Bi (JCPDS card file, No. 44-1246) and PbTe (JCPDS card file, No. 78-1904), respectively. It can be seen from Fig. 1(a) that the (0 1 2) plane peak of the Bi is relative stronger than that of the standard data. The ratio between the intensities of the (0 1 2) and (1 1 0) (the second strong) plane peaks, $I_{(0\,1\,2)}/I_{(1\,1\,0)}$ is 7.4, which is higher than that of the standard data ($I_{(0\,1\,2)}/I_{(1\,1\,0)} = 3.45$), indicating that the Bi film is (0 1 2)-textured. For the PbTe film, the ratio between the intensities of the strongest (2 0 0) plane peak and the second strong (2 2 0) plane peak is 4.79 (see Fig. 1(b)). It is also higher than that of the standard data (1.42). This indicates that the PbTe film is (2 0 0)-textured.

Typical XRD patterns of samples IIIA, IIIB, and IIIC are shown in Fig. 2. It can be clearly seen from Fig. 2(a) that sample IIIA consists of elemental Bi and Te. Fig. 2(b) shows that sample IIIB consists of $Bi_2Te_3$, Bi and Te. It can be seen from Fig. 2(c) that all the diffraction peaks except the peak for Si(1 1 1) can be indexed to the reported $Bi_2Te_3$ (JCPDS card file, No. 85-0439), indicating that pure $Bi_2Te_3$ film was prepared under this condition. As samples IIIA and IIIB were not $Bi_2Te_3$ or containing impurities, further examination on these samples were not performed.

Typical FE-SEM images of the samples I, II and IIIC are shown in Fig. 3. It can be seen from Fig. 3(a) that the Bi film is smooth and dense. The film contains many nanocracks, which must be caused during the drying procedure. Fig. 3(b) shows that the PbTe film is also very dense and contains big dendritic patterns, which is probably because some PbTe nuclei grew up quickly driven by centrifugal force. Such dendritic structures were also observed in the PbTe film prepared by electrodeposition [14]. It can be seen from Fig. 3(c) that there are some rod-like structures (~10 nm in diameter and 500 nm in length) within the film of sample IIIC, which should be formed during the annealing process. Besides, the $Bi_2Te_3$ film also has some nanocracks (~1 to 2 μm in length and 30–100 nm in width).

The reaction process for the formation of the Bi film is proposed as follows:

$$Bi^{3+} + 2C_4H_4O_6^{2-} \Rightarrow (Bi \cdot 2C_4H_4O_6)^- \quad (1)$$

$$2(Bi \cdot 2C_4H_4O_6)^- + 6BH_4^- \Rightarrow 2Bi + 4C_4H_4O_6^{2-} + 3B_2H_6\uparrow + 3H_2\uparrow \quad (2)$$

The $Bi^{3+}$ in solution was complexed by sodium tartrate and $(Bi{\cdot}2C_4H_4O_6)^-$ formed according to reaction (1). Both the $(Bi{\cdot}2C_4H_4O_6)^-$ and the $BH_4^-$ are negative charges, therefore, the reduction reactions related to them were relative difficult in the precursor solution. When the precursor drops were being spin-coated, the charge equilibrium was destroyed and the $(Bi{\cdot}2C_4H_4O_6)^-$ was quickly reduced into Bi nuclei by $BH_4^-$ to form Bi film on the Si wafer (reaction (2)). Other impurity ions in the film were soluble and could be removed by rinsing in deionized water.

As the precursor of sample II is similar to that for PbTe film prepared by chemical bath deposition (CBD), we propose they

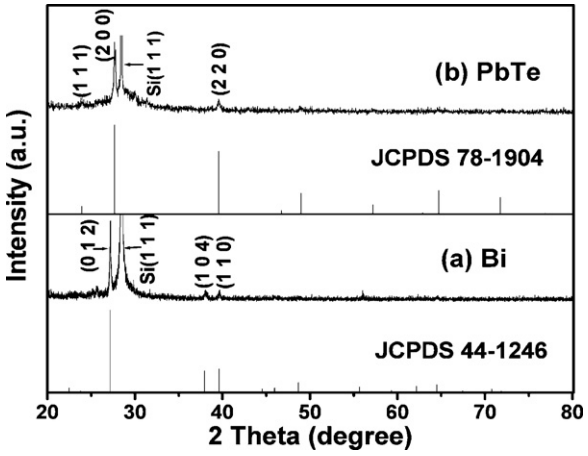


Fig. 1. XRD patterns of (a) sample I and (b) sample II deposited on Si(1 1 1) substrates at room temperature.

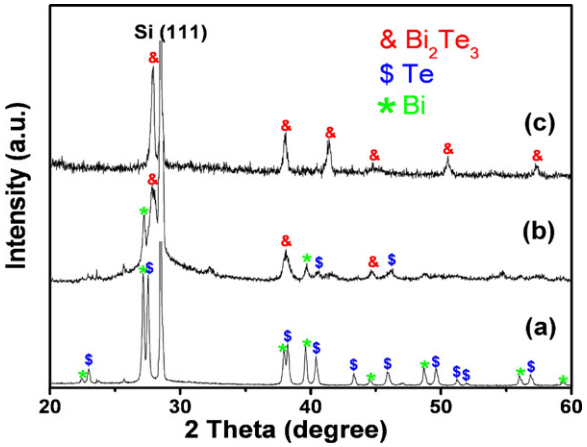


Fig. 2. XRD patterns of (a) sample IIIA, (b) sample IIIB, and (c) sample IIIC deposited on Si(1 1 1).

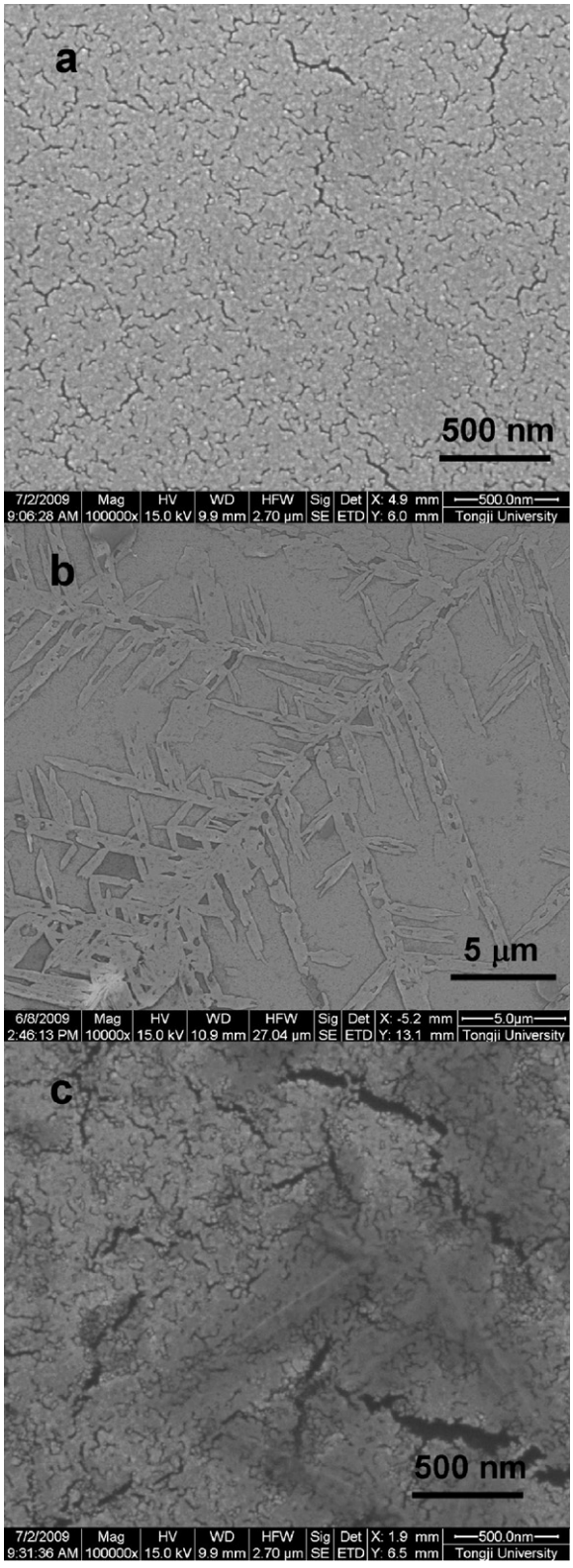


Fig. 3. Typical FE-SEM images of the surface morphology of (a) sample I; (b) sample II; and (c) sample IIIC deposited on Si(1 1 1) substrates.

have the same reaction mechanism, which is described as follows [17]:

$$Pb^{2+} + 3OH^- \Rightarrow HPbO_2^- + H_2O \quad (3)$$

$$TeO_2 + 2OH^- \Rightarrow TeO_3^{2-} + H_2O \quad (4)$$

$$HPbO_2^- + H_2O \Leftrightarrow Pb^{2+} + 3OH^- \quad (5)$$

$$Pb^{2+} + TeO_3^{2-} \Leftrightarrow PbTeO_3 \quad (6)$$

$$2PbTeO_3 + 6BH_4^- \Rightarrow 2PbTe + 6OH^- + 3B_2H_6\uparrow \quad (7)$$

The $Pb(Ac)_2$ and $TeO_2$ dissolved in excess alkali solution and formed $HPbO_2^-$ and $TeO_3^{2-}$ ions, according to reactions (3) and (4), respectively. Some $HPbO_2^-$ ions were hydrolyzed into $Pb^{2+}$ (reaction (5)), and then combined with $TeO_3^{2-}$ to form $PbTeO_3$ colloidal particles (reaction (6)), which were reduced by $BH_4^-$ to form PbTe film (reaction (7)). As the charge equilibrium of precursor was broken during the spin-coating process, the formation of PbTe film was much faster than that prepared by the CBD method [17].

For the $Bi_2Te_3$ film, elemental Bi and Te were first formed in stoichiometric ratio as the precursor was spin-coated according to reactions (2) and (8):

$$TeO_3^{2-} + 4BH_4^- + 3H_2O \Rightarrow Te\downarrow + 6OH^- + 2B_2H_6\uparrow + 2H_2\uparrow \quad (8)$$

The Bi atoms reacted with Te atoms to form $Bi_2Te_3$ during the annealing. The cracks formed in the film are probably because of the heating rate used for annealing being too fast.

Electrical conductivities of the Bi, PbTe, and $Bi_2Te_3$ films are 5.12, 2.55, and 17.6 S $m^{-1}$, respectively. These values are lower than those of corresponding bulk materials. This should be because these films mainly consist of nanoparticles, which will have strong grain boundaries scattering of carriers. Nevertheless, extremely low thermal conductivity for the film could be expected due to strong grain boundaries scattering to the phonons, which is beneficial to the *ZT* value.

## 4. Conclusions

In summary, Bi, PbTe, and $Bi_2Te_3$ thermoelectric thin films were prepared via spin-coating corresponding metastable precursors. The Bi and PbTe films are dense and smooth, while the $Bi_2Te_3$ film has some nanocracks due to annealing. This technique is convenient, low cost and can be extended to other semiconductor thin films. The electrical conductivities of the films are very low due to the effect of grain boundaries scattering.

## Acknowledgements

This work was supported by National Natural Science Foundation of China (50872095) and the 973-Project under Grant No. 2007CB607500.

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