Synthesis and Characterization of CNTs/Bi$_2$Te$_3$ Thermoelectric Nanocomposites

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Multi-walled carbon nanotubes (MWNTs)/Bi$_2$Te$_3$ composite thermoelectric films were prepared by potentiostatic electrodeposition at room temperature. The morphology, composition and electrical resistivity of the films were analyzed by environment scanning electron microscopy (ESEM), energy dispersive spectroscopy (EDS), and four-probe resistivity measuring device. Effect of the concentration of MWNTs in the electrolyte on the electrical resistivity of the composites was also evaluated. The results show that the resistivity of the composites films decreases remarkably at the present of MWNTs. This effect turns to be more notable at more negative deposition potentials due to the increase of composited MWNTs. In the process of adding more MWNTs into the electrolytes, the resistivity of the composites decreases first and then achieves stable. The optimum of resistivity as 0.93×10^{-5} Ω·m was obtained at the deposition potential of -0.07V, the added amount of MWNTs is equal to or greater than 3mg/ml. This work suggests a new method to improve thermoelectric properties of Bi$_2$Te$_3$ based materials.

1. INTRODUCTION

Thermoelectric materials and cells have attracted considerable interest due to the requirements of environment protection and military application. Good thermoelectric materials should possess large Seebeck coefficient (S), low thermal conductivity (σ) and low electrical resistivity (ρ). Generally, the performance of thermoelectric materials can be expressed by the dimensionless quantity ZT ($ZT = S^2/\sigma\rho$) where T is the temperature and Z is the thermoelectric figure of merit[1,2]. The thermoelectric conversion efficiency of thermoelectric materials increases with the increase of ZT.

Bi_2Te_3-based materials are of great interest for thermoelectric applications in the temperature range of 200–400 K. In general, Bi_2Te_3- based film materials can be fabricated by chemical vapor deposition (CVD) [3], physical vapor deposition (PVD) [4], electrodeposition[5-7] , and so on. Compared to traditional techniques, electrodeposition shows many advantages as simple device, low cost and easy operation. The most advantageous point of the electrodeposition is high controllability as the doping concentration and crystalline state of thermoelectric films can be easily controlled through adjusting the parameters of electrodeposition. Nowadays, the electrodeposition of bismuth telluride, bismuth antimony telluride and bismuth selenium telluride from aqueous [8-10] or nonaqueous solutions [11, 12] has been a topic of recent experimental research.

Carbon nanotubes(CNTs) are renowned for their extraordinary electrical, mechanical and thermal properties, and are widely used as dopant to synthesize functional materials. Such as CNTs introduced into Cr coating to enhance its mechanical properties[13], into Cu coating to increase the electrical conductivity and wear resistance[14], into epoxy resin or ceramics to optimize the electrical conductivity[15], into conducting polymers to improve its membrane separation[16], and so on. Furthermore, CNTs are likely to achieving a high *ZT* due to its nanosize and holey structure features. Consequently, they are promising candidates for TE materials in view of the quantum confinement effect of the charge carriers and the size effect of the heat carriers[17]. Recently, there has been some reports about the introduction of CNTs will improve the thermoelectric performance of conducting polymers[18] or Bi_2Te_3-based materials[19] by enhance the electrical conductivity dramatically while maintain the thermal conductivity and Seebeck coefficient stable. CNTs composite materials can be prepared by various methods. But to fabricate CNTs/Bi_2Te_3 based composite thermoelectric materials by electrodeposition has not been reported yet. In this article, MWNTs/Bi_2Te_3 composite thermoelectric films were prepared by potentiostatic electrodeposition technique. The morphology, composition and electrical resistivity of the films were analyzed. The effect of the volume of MWNTs added into the electrolyte on the electrical resistivity of the composites was also discussed here.

2.EXPERIMENTAL

MWNTs (Shenzhen Nanotechnologies Co. Ltd.) were about 2-8 nm in outer diameter and 0.5-2 μm in length (95% purity). They were acid treated in a solution of 1:3 (v:v) nitric acid/ sulfuric acid at 80 ℃ for 1.5 h then collected on 0.45 μm filter, rinsed with distilled water to pH keeps stable, and dried at 60 ℃ for 4 h. The basic electrolyte for the electrodeposition of Bi_2Te_3 films was composed of $Bi(NO_3)_3 \cdot 5H_2O$ (4.85g/L), K_2TeO_3 (2.54g/L), KNO_3 (100g/L)and HNO_3 (67ml/L)(Shanghai Chemical Reagent Company). Electrolytes for the fabrication of MWNTs/Bi_2Te_3 films were prepared by adding 0.5,1,2,3 or 4 mg/ml of purified MWNT into the basic electrolyte, and then an ultrasonic field (40 kHz, 100 W) was applied to mix the electrolytes for 2 h.

Bi_2Te_3 films and MWNTs/Bi_2Te_3 composite films were electrochemically deposited on nickel plate by potentiostatic electrodeposition using CHI660D electrochemical working station. The counter electrode and reference electrode were Pt foil and SCE, respectively. The average thickness of the deposited films was 20 μm.

The morphology of the deposit was analyzed using environment scanning electron microscope (ESEM, Nanosem 430). The chemical composition of the deposit was analyzed using the energy dispersive spectrometer (EDS) (EDAX) attached on the ESEM. The electrical resistivity of the deposited thermoelectrical films were measured by the four-probe resistivity measuring device (TJU-EC2002) developed by Tianjin University at 25±1 ˚C. Before the characterization of electrical property, the deposited films were firstly peeled off from the Ni substrate using epoxy resin and annealed at 250 ℃ for 2 h under N_2 atmospheric pressure condition.
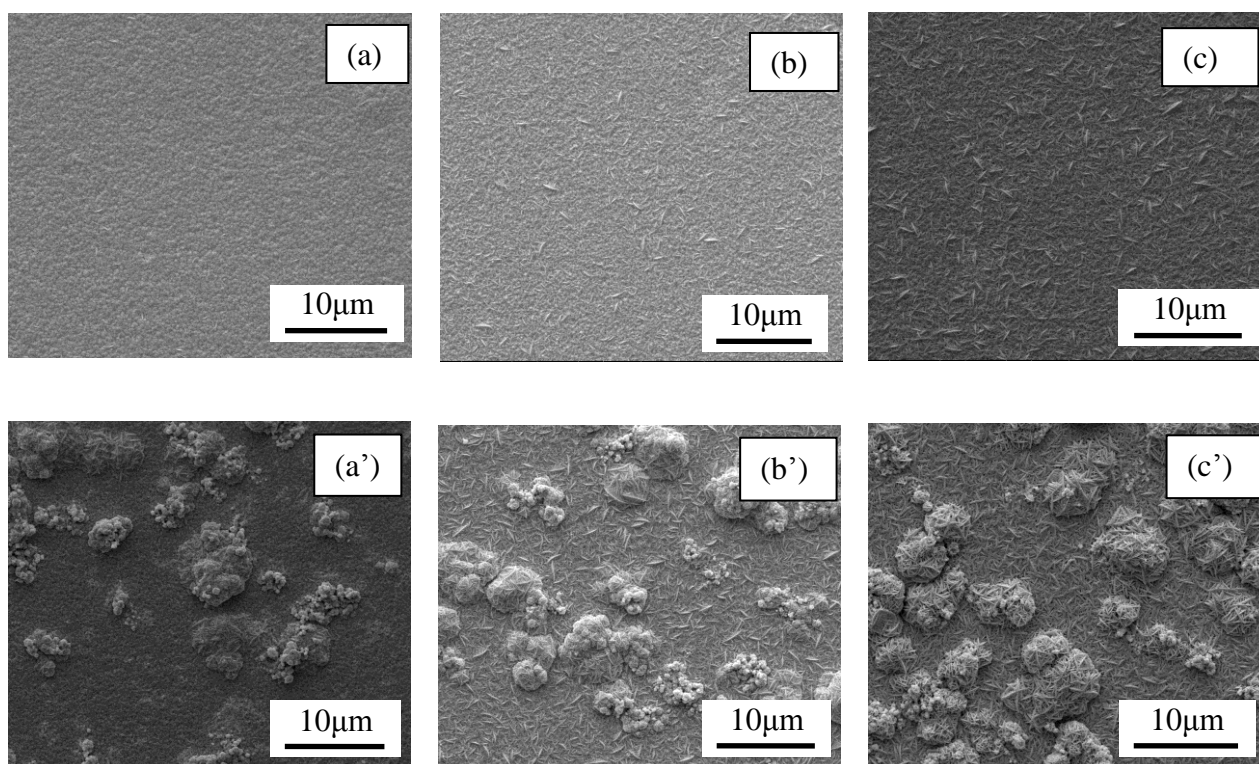
3. RESULTS AND DISCUSSION

Figure 1. SEM images of Bi_2Te_3 films (a),(b),(c) and MWNTs/Bi_2Te_3 composite films (a'),(b'),(c') electrodeposited at 0.02V,-0.02V and -0.07V, respectively.

Fig. 1 shows the SEM images of Bi_2Te_3 films and MWNTs/Bi_2Te_3 composite films electrodeposited at different potentials in the bath containing 0.5mg/ml MWNTs. Both two kinds films are dense films and turn to be rough as the deposition potential shifts negatively due to the concentration polarization raises gradually. Several salient appears on the surface of MWNTs/Bi_2Te_3 composite films, which is caused by the bundles of MWNTs as the co-deposition of MWNTs introduces new nucleation sites of Bi_2Te_3 compound. The amount of salient increases while the deposition potential shifts negatively. It can be attributed to that the more rapid deposition rate corresponding to more negative potential is beneficial to the embedding of MWNTs. At the same time, it can be obtained that the morphology of the smooth zone on the composites are almost the same as

that of Bi_2Te_3 films, which indicates that the introduction of MWNTs doesn't affect the formation of matrix of Bi_2Te_3 compound.
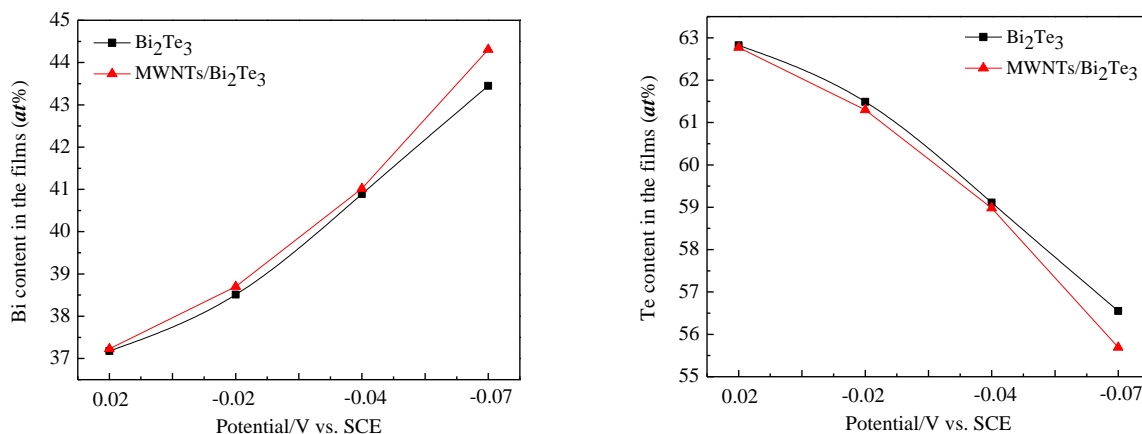

Figure 2. Variation of composition of Bi_2Te_3 films and MWNTs/Bi_2Te_3 composites with the electrodeposition potential (the concentration of MWNTs in the electrolyte is 0.5mg/ml).

The variation of composition of Bi_2Te_3 films and MWNTs/Bi_2Te_3 composites with the electrodeposition potential is shown in Fig.2. It can be seen that the Bi content in both two kinds of films increases with the deposition potential shifts negatively, while the variation of Te content shows opposite trend.
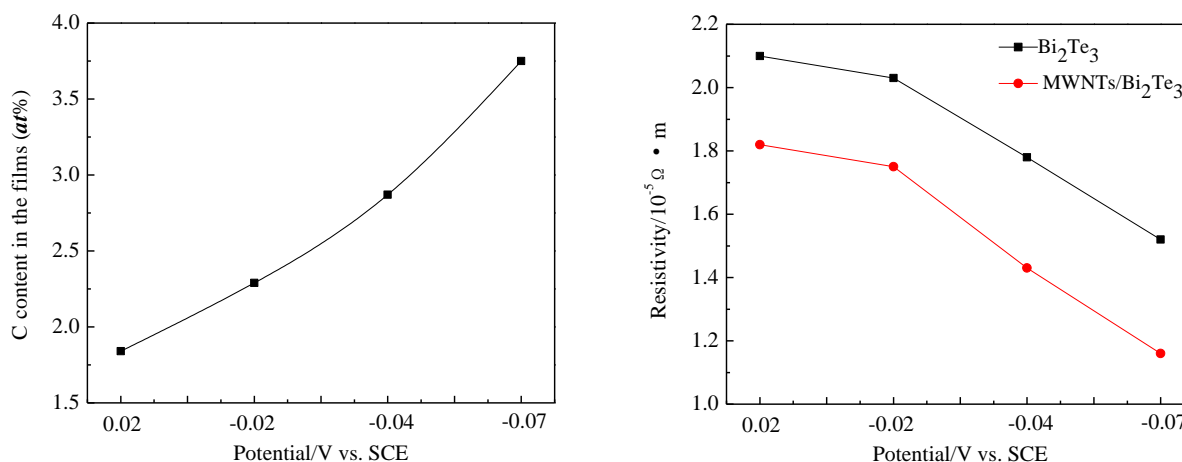

Figure 3. Variation of C content in MWNTs/Bi_2Te_3 composites and the electrical resistivity of Bi_2Te_3 films and MWNTs/Bi_2Te_3 composites with the electrodeposition potential.

This result is consistent with the conclusion of our previous work, which described that the formation of Bi_2Te_3 compound could be divided into two processes[20]. The first one is reduction of Te onto substrate, and the second one is the reaction of Bi^{3+} and Te to form Bi_2Te_3 compound. As discussed in another work of our group[21], the introduction of MWNTs doesn't affect the formation of Bi_2Te_3 compound but increase the rate of this process. As a result, MWNTs/Bi_2Te_3 composite films

possess almost the same composition as that of Bi_2Te_3 films, which confirms that the introduction of MWNTs don't affect the formation of matrix of Bi_2Te_3 compound again. The slight difference of the composition caused by the addition of MWNTs may be attributed to the special porous structure of MWNTs affects the adsorption of inorganic irons.

Fig.3 shows the variation of C content and resistivity with the electrodeposition potential. The content of C content in the composites is calculated by C2%-C1%, where C2% and C1% are corresponding to C content detected from composite films and blank films, respectively. It can be seen that the C content increases as the deposition potential shifts negatively, which indicates that more MWNTs are embedded into the composites due to the more rapid deposition rate at more negative potential. This conclusion is consistent with the morphology analysis of SEM images. As an inevitable result of the above trend, the resistivity decreases remarkably while the potential shifts negatively, which shows that the introduction of MWNTs is helpful to reduce the resistivity of composites.

Fig.4 shows the variation of C content and electrical resistivity of MWNTs/Bi_2Te_3 composites deposited at -0.07V with the MWNTs concentration in the electrolyte. With the increase of MWNTs concentration in the bath, the C content in the MWNTs/Bi_2Te_3 composites increases first and then achieves a stable value, while the resistivity of the composites decreases first and then also gets stable. It is due to that when the concentration of MWNTs in the bath is less than 3mg/ml, more MWNTs in the electrolyte are in favor of increasing the embedding amount of MWNTs in the composites. But when the concentration of MWNTs keeps increasing, some of them will agglomerate with each other, then cause the effective concentration of MWNTs maintains stable. It can be obtained that the optimum of resistivity as 0.93×10^{-5} $\Omega \cdot m$ was obtained at the deposition potential of -0.07V when the concentration of MWNTs is equal to or greater than 3mg/ml.
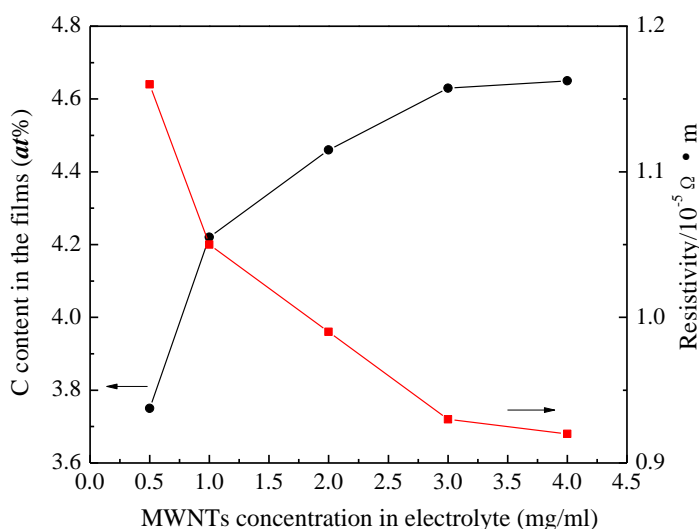

Figure 4. Variation of C content and electrical resistivity of MWNTs/Bi_2Te_3 composites with the MWNTs concentration in the electrolyte (deposited at -0.07V).

4.CONCLUSION

MWNTs/Bi$_2$Te$_3$ composite thermoelectric films were prepared by potentiostatic electrodeposition at room temperature. The morphology, composition and electrical resistivity of the films were analyzed. The results show that the introduction of MWNTs doesn't affect the formation of matrix of Bi$_2$Te$_3$ compound but is helpful to reduce the electrical resistivity of the films. Salient appears on the surface of MWNTs/Bi$_2$Te$_3$ composite films due to the embedding of MWNTs. As the deposition potential shifts negatively, the amount of MWNTs in the films increases while the resistivity of the films decreases gradually. With the increase of MWNTs concentration in the bath, the C content in the MWNTs/Bi$_2$Te$_3$ composites increases first and then achieves a stable value, while the resistivity of the composites decreases first and then also gets stable. The optimum of resistivity as 0.93×10^{-5} $\Omega \cdot$m was obtained at the deposition potential of -0.07V when the concentration of MWNTs is equal to or greater than 3mg/ml.

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