Bi_2Te_3 THERMOELECTRIC FILMS BY ELECTRODEPOSITION FROM DMSO-WATER MIXTURES

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Abstract: Bi_2Te_3 films were electrodeposited from DMSO-water mixtures. The addition of water was proven to enhance the conductivity by a factor of 6 compared to that of pure DMSO solutions, while still maintain high solubilities of Bi and Te species. Bismuth telluride films with smooth morphology could be prepared at deposition rates up to 100 µm/h. Composition of the films could be controlled either by varying the applied current or by adjusting the bath composition. SEM and EDX investigation on the cross-section showed that the film thickness was uniform over the substrate and composition remained constant across the depth. Both n-type and p-type Bi_2Te_3 films could be obtained with Seebeck coefficients up to -50 and +30 µV/K, respectively.

Keywords: bismuth telluride, thermoelectric films, electrodeposition, DMSO-water mixtures

INTRODUCTION

Bismuth telluride (Bi_2Te_3) films are well-known as the best materials for thermoelectric applications around room temperature. Bismuth telluride films have been prepared by various techniques, such as physical vapor deposition (PVD) or chemical vapor deposition (CVD), which provide relatively low deposition rate and high internal stress. Electrodeposition is known as a fast, low temperature and low-cost technique to prepare films, and compatible with MEMS fabrication process. Up to date, electrodeposition of Bi_2Te_3 is mostly carried out from nitric acid solutions [1–4], in which only low concentrations of bismuth and tellurium species can be dissolved, thus limiting the deposition rate. Recently, Li [5] proved a possibility to deposit Bi_2Te_3 films from a DMSO electrolyte containing 0.01 M $TeCl_4$ and 0.0075 M $Bi(NO_3)_3$. Although DMSO solutions are capable of dissolving much more bismuth and tellurium ions, our preliminary work revealed that conductivity of these electrolytes was low and addition of conducting salts did not improve the conductivity significantly. This poor electrolyte conductivity may result in non-uniform current distribution over the substrate, and so non-uniform film thickness.

In this paper, we report the use of dimethyl sulfoxide (DMSO) - water mixtures as electrolytes for the electrodeposition of bismuth telluride thermoelectric films. It is found that addition of water enhances the electrolyte conductivity, while still maintaining high solubility of Bi and Te species. Smooth morphology and stoichiometric Bi_2Te_3 films could be prepared at growth rates, theoretical up to 100 µm/h.

EXPERIMENTS

Different DMSO-water mixtures were prepared by dissolving $Bi(NO_3)_3.5H_2O$ and $TeCl_4$ in pure DMSO and then adding water. Electrical conductivity of the solutions was determined via impedance measurement, performed by Autolab potentiostat. Linear sweep voltammograms (LSV) were recorded by an EG&G 273 potentiostat.

Bi_2Te_3 films were prepared on Pt- or Au-coated silicon wafers (0.7×1.5 cm), which rotated at 400 rpm, under galvanostatic mode at room temperature.

Morphology and composition of the deposited films were examined by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively. Seebeck coefficient measurements were carried out on 1x2.5 cm^2 samples.

RESULTS AND DISCUSSION

Effect of water content

In order to test the effect of water content on electrolyte conductivity, several solutions containing 0.2 M $Bi(NO_3)_3$ and 0.16 M $TeCl_4$ were prepared. The first solution contains 1.8 vol.% of water, which was from the hydrated water in the Bi-salt. In other solutions, water was added to 10, 20 and 30 vol.%. Solutions with higher water content were not examined because precipitation was formed gradually. Conductivity of the solutions is calculated from impedance measurements, carried out by frequency response analyzer (FRA, integrated in Autolab potentiostat). As showed in Fig. 1, the conductivity of

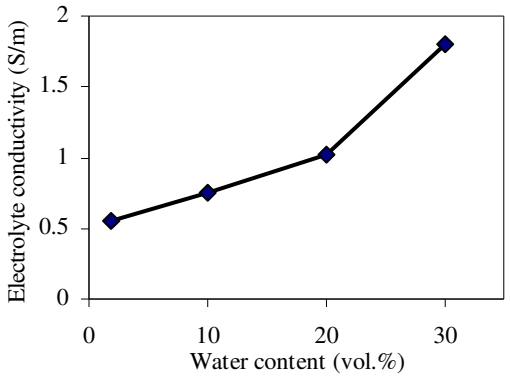

Figure 1. Conductivity of water-DMSO mixtures at different water content (with 0.2 M $Bi(NO_3)_3$ and 0.16 $TeCl_4$)

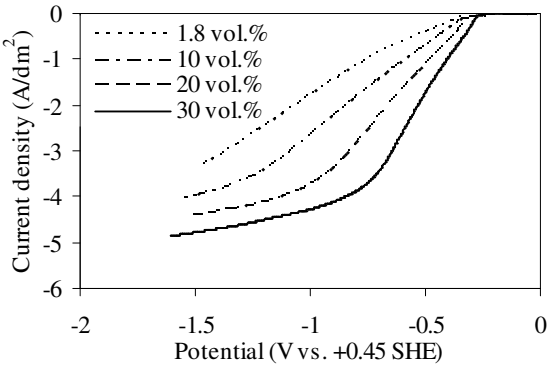

Figure 2. Linear sweep voltammograms of electrolytes with different water contents (with 0.2 M $Bi(NO_3)_3$ and 0.16 $TeCl_4$, room temperature).

the solutions increases from 0.56 to 1.8 $(\Omega m)^{-1}$ as the water content increases from 1.8 to 30 vol.%. This dramatic change may be explained by the changes in type and concentration of conducting ions in the solutions. In water-free DMSO solutions, bismuth and tellurium ions are complexed by chloride ions. The form of the complexes can be Bi^{3+}, $BiCl^{2+}$, $BiCl_2^{+}$, Te^{4+}, $TeCl_3^{+}$, $TeCl_2^{2+}$, $TeCl_3^{+}$, $TeCl_5^{-}$, $TeCl_6^{2-}$, depending on the chloride concentration [6]. In presence of water, those complexed ions may be replaced by oxygen-containing ions, BiO^{+} and $HTeO_3^{-}$ (those ions are formed if neutral water is added, according to the Pourbaix diagrams of bismuth and tellurium [7]), releasing free chloride Cl^{-} ions and protons. As a result, the conductivity of the solutions is enhanced. Fig. 2 shows linear sweep voltammograms (LSV) measured from the DMSO-water mixtures with different water contents. It is observed that the LSV corresponding to the solution containing 30 vol.% water has the highest current.

Electrodeposition of Bi_2Te_3 films

Electrodeposition of bismuth telluride films from DMSO-water mixtures was carried out at constant currents. From the solution containing 30 vol.%, shiny films could be prepared when the thickness was less than about 3 μm. The films cracked and peeled off at higher thickness due to high internal stress. The internal stress in the deposited films is suggested to concern about the reduction of oxygen-containing ions of bismuth and tellurium, as mentioned above, which are more difficult to be reduced than the free or chloride-complexed ones (Bi^{3+}, Te^{4+}, $BiCl_y^{(3-y)}$, or $TeCl_x^{(4-x)}$).

Thick films could be deposited from solutions containing 20 vol.% or less water, although delamination around the edge was observed for the films from the solution with 20 vol.% H_2O. From solutions containing 10 and 1.8 vol.% water, the films appeared to be inhomogeneous with large thickness at the edges around the substrate, which is due to the larger current density at the edge of the substrate. In this case, the problem might be more serious because of low conductivity of the electrolyte. So, 20 vol.% H_2O can be considered the optimized content of water in DMSO-water mixtures as electrolytes for Bi_2Te_3 deposition.

Electrodeposition of several bismuth telluride films were carried out from two solutions (20 vol.% water) containing 0.2 M $Bi(NO_3)_3$, 0.16 M $TeCl_4$ and 0.1 M $Bi(NO_3)_3$, 0.1 $TeCl_4$ on Pt- and Au-coated silicon wafers (rotating at 400 rpm), at different current densities, at room temperature (see Table 1). All the obtained deposits are uniform and shiny, as illustrated in Fig. 3. The surface morphology is much smoother than that observed for films deposited from nitric acid electrolytes or from pure DMSO electrolytes obtained by Li [5].

Table 1. Bi_2Te_3 films prepared at different current density on Pt- and Au- coated substrates (Solution: DMSO-20 vol.% water

Solution	Sample	Substrate	Current density (A/dm^2)	Film composition (at. % Te)
0.2 M $Bi(NO_3)_3$, 0.16 M $TeCl_4$	1	Pt/Si	5	61.2 ± 1.8
	2	Pt/Si	4	61.5 ± 1.2
	3	Pt/Si	3	61.5 ± 1.4
	4	Au/Si	2	62.8 ± 1.1
	5	Au/Si	3	59.1 ± 1.3
0.1 M $Bi(NO_3)_3$, 0.1 $TeCl_4$	6	Au/Si	0.5	82.8 ± 1.3
	7	Au/Si	1	66.2 ± 0.9
	8	Au/Si	2	61.1 ± 1.8
	9	Au/Si	5	57.6 ± 2.0

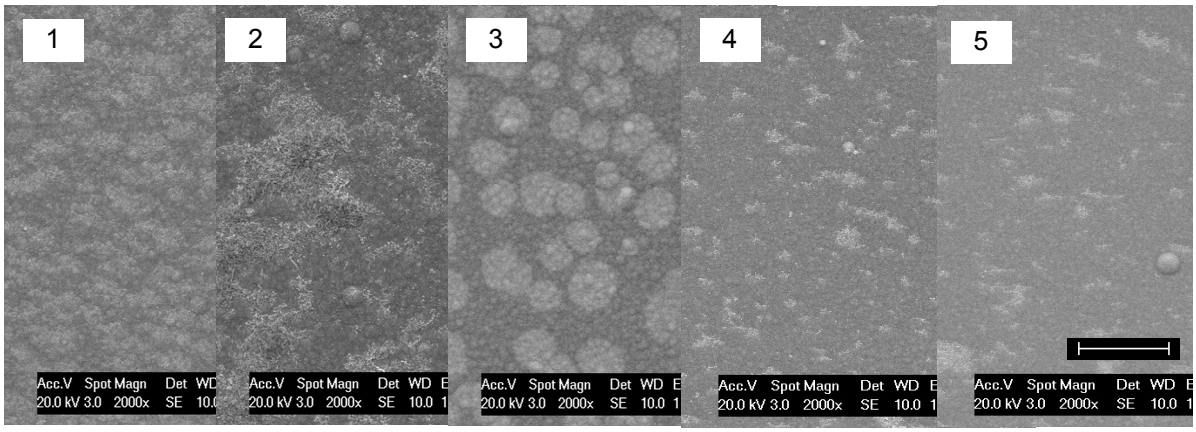

Figure 3. Morphology of Bi_2Te_3 films deposited from DMSO-water electrolytes containing 20 vol.% of water, 0.2 M $Bi(NO_3)_3$ and 0.16 $TeCl_4$. Conditions: room temperature, rotating disk 400 rpm. Compositions of the films are given in Table 1 (scale bar 10 μm).

From the solution containing 0.2 M Bi, 0.16 M Te, EDX analysis revealed that close stoichiometric composition could be achieved for the films deposited at different deposition current densities, as summarized in Table 1. This observation agrees with the result obtained by Li [5], where the film composition was found to be independent of the applied potential. From the solution containing 0.1 M Bi, 0.1 M Te, a film with 82.8 at.% of Te was obtained at low current density.

Cross-section of the sample 9 (see Table 1) was examined by SEM and EDX. As showed in Figure 4, the film is compact without cracks. Examination over the sample revealed uniform thickness. Composition profile performed across the depth of the film showed consistent values.

Seebeck coefficient measurements showed that negative values, -10 to -50 μV/K, were observed for all films with composition close to stoichimetric (samples 1 – 5 and 7 – 9, Table 1). Positive Seebeck coefficient of +30 μV/K was observed for sample 6 (with 82.8 at.% of Te). This observation agrees with the result presented in [6].

CONCLUSION

DMSO-water electrolytes were investigated for the electrodeposition of Bi_2Te_3 films. Compared to the conventional nitric acid plating baths, the concentrations of Bi and Te species are far higher, which allows to deposit bismuth telluride films at very high current density (calculated growth rate of 100 μm/h). This is definitely an advantage in fabrication of vertical thermopiles, where thickness of about 100 μm is required. Furthermore, compared to pure DMSO solutions, DMSO-water mixtures provide better film uniformity due to the higher conductivity.

Both n-type and p-type thermoelectric films can be prepared from one solution, by varying applied current (potential), which simplifies the fabrication process for thermopiles, or by varying the bath composition.

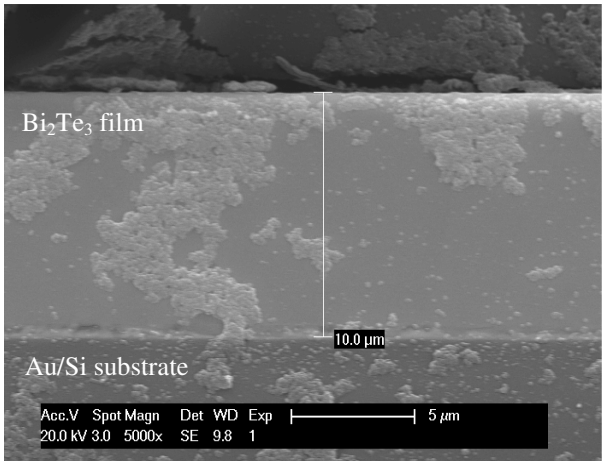

Figure 4. Cross section of sample 9 (see Table 1). Composition (depth profile) was checked by EDX along the dimension marker.

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