Electrochemical deposition of Bismuth Telluride Thick layers onto Nickel

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Abstract

Bismuth telluride (Bi_2Te_3) is the currently best performing thermoelectric (TE) material in commercial TE devices for refrigeration and waste heat recovery up to 200°C. Up to 800 μm thick, compact, uniform and stoichiometric Bi_2Te_3 films were synthesized by pulsed electrodeposition from 2M nitric acid baths containing bismuth and tellurium dioxide on 1cm^2 nickel (Ni) substrates at average film growth rates of ~50 μm/hour. Pre-treatment of the Ni substrate was found to significantly enhance the adhesion of Bi_2Te_3 material onto Ni whilst pulsed electrodeposition was used to increase the compactness of the material. To maintain a homogeneous composition across the thickness of the films, a sacrificial Bi_2Te_3 anode was employed. All deposits produced were n-type with a Seebeck coefficient of up to -80μV/K and an electrical conductivity of ~330 S/cm at room temperature.

1. Introduction

Thermoelectric (TE) generators are devices that can directly convert heat into useful electrical energy using the Seebeck effect. TE generators have a number of advantages that include solid state electrical components, high reliability and silent operation with long service free lifetimes with zero emissions. One of the main disadvantages of existing TE generators is their low conversion efficiency, which is mainly due to the low efficiency of the TE materials embedded in them. Commercially available bismuth telluride (Bi_2Te_3) based TE

devices have an efficiency of ~10% [1] and are one of the best materials for Peltier coolers and TE devices operating near room temperature [2, 3].

Electrochemical deposition provides an attractive route to the fabrication of high-quality TE materials such as bismuth telluride, offering several advantages over other methods. These include low cost, high controllability over size, thickness, crystallinity [4], scalability, room-temperature fabrication, and fast deposition rate which are suitable for producing thick films that can be incorporated into practical TE devices. To harvest thermal energy more effectively, thick Bi_2Te_3 films are required as thick layers for practical TE devices (≥300 μm) [5-7]. However, to obtain uniformly thick Bi_2Te_3 films by electrodeposition still represents a significant challenge due to a number of factors: the Bi_2Te_3 film tends to crack due to the built-up of internal stress as the thickness increases; constant stoichiometry over the entire thickness is compromised due to the change in the precursors' concentration in the electrolyte bath as deposition progresses; and the surface tends to be rougher as the thickness increases. To achieve the growth of Bi_2Te_3 thick films a number of strategies have been employed which include the use of pulsed electrodeposition [8] and the use of a soluble Bi_2Te_3 anode [9].

There is considerable interest to deposit Bi_2Te_3 directly onto nickel (Ni) substrates, as Ni acts as a diffusion barrier in commercial TE devices that prevents diffusion of Sn from the solder and Cu from the electrode into both p- and n-type Bi_2Te_3 legs [3]. Electrodeposition of Bi_2Te_3 has mostly been carried out from nitric acid based electrolytes [10, 11], which is challenging if Ni is used as a substrate as nitric acid will etch the Ni surface. There are indeed very few reports for the electrodeposition of Bi_2Te_3 onto Ni [12, 13] and this study represents the first study in which extremely thick layer deposition >500 μm was achieved.

In this report, we describe the optimised electrochemical deposition conditions that were employed to produce uniform and compact and well adherent Bi_2Te_3 layers on Ni with thicknesses > 500 μm of stoichiometric composition that displayed excellent thermoelectric performance.

2. Experimental

2.1. Materials

All solutions were prepared using water from a Purite Select Fusion 160 (Ondeo) water purification system with a resistivity of 18.2 MΩ cm. Bi powder (Alfa Aesar, 99.5%), Te powder (Alfa Aesar, 99+%), TeO_2 powder (Alfa Aesar, 99.99%), Ni foil (Alfa Aesar, 0.127mm thick, 99+%) and HNO_3 (Fisher, 70%) were used as received. The electrolyte solution consists of 70 mM TeO_2 and Bi with a ratio of [Bi]/[Te]=0.75-1.2, dissolved in 2M HNO_3. The maximum concentration of TeO_2 that could be dissolved in 2M HNO_3 was found to be ~70 mM even though a value of up to 80 mM was previously reported in the literature [8].

2.2. Film fabrication by electrodeposition

All electrochemical experiments were performed using a standard three-electrode configuration, where a large-area platinum grid and saturated calomel electrodes (SCEs) were used as counter and reference electrodes, respectively. Instead of using a large piece of Bi_2Te_3 as the counter electrode as reported in paper [8], a small (~0.2cm^2) piece of a Bi_2Te_3 ingot is attached to a Pt grid by Pt wire and serves as a sacrificial anode. This was found to replenish bismuth and tellurium ions during electrodeposition. The working electrode is a Ni foil with a masked electrode area of 1cm^2 area. Prior to electrodeposition, Ni foil substrates are etched in concentrated HCl solution for 1min, followed by anodic etching in 1M HNO_3 at a potential of

+0.15 V vs SCE for 30 seconds. The etched Ni electrode is then washed with deionized water and immersed into the bismuth telluride electrolyte bath without drying. Electrochemical etching of the Ni substrate was found to significantly improve the adhesion of bismuth telluride to the Ni substrate as it resulted in a stronger bonding between metallic Te or Bi and Ni than with Ni oxide. The electrodes were connected to a computer-controlled potentiostat/galvanostat (Ivium Technologies). The electrolyte bath contained 30 ml electrolyte which was stirred with a magnetic stir bar at 500 rpm. Electrodeposition is carried out by pulsed deposition employing zero current resting pulses of 2-5s and deposition pulses of 10-100 ms at -0.01 to -0.06 V vs. SCE.

The morphology and chemical composition of the deposited films was analyzed by scanning electron microscope (SEM, JSM 5910) and energy dispersive X-ray (EDX, Oxford Inca 300) respectively. EDX compositional analysis had an accuracy of 5%. X-ray diffraction (XRD) data were obtained using a Rigaku SmartLab instrument with Cu Kα radiation ($\lambda = 1.5406$Å). The electrical transport properties of the deposited films were measured along the film plane using the standard van der Pauw technique with a direct current (DC) of 19 mA and a permanent magnetic field of 0.37 T at room temperature using a commercial Hall effect measurement system (HMS 300 from Ecopia). Prior to Hall effect measurements, each deposit was delaminated from the Ni substrate by embedding it into an epoxy resin matrix, in order to remove any contribution from the metallic substrate to the electronic measurements of the deposits. Commercial 0.2mm thick copper wires (from RS Ltd.) were soldered onto each corner of the squared sample using a silver epoxy resin (circuitworks) to make good Ohmic contact. The thermoelectric Seebeck coefficient S (μV/K) was determined using a custom-made Seebeck measurement unit, which was calibrated against a polycrystalline Bi foil reference standard. The measurement accuracy was found to be within 5%, and the

system was calibrated using copper-constantan thermocouples and a high precision Keithley DMM 2000/E digital multimeter with 0.1% accuracy.

3. Results and discussion

Figure 1 shows representative cyclic voltammograms for bismuth telluride electrodeposition recorded at a 1cm^2 Ni foil working electrode immersed in electrolyte solutions containing 2M HNO_3 + 70mM TeO_2 + 70mM Bi^{3+} at a scan rate of 20 mV/s. The potential was swept from +0.5V to -0.4V *versus* a SCE reference electrode. A small oxidation peak appeared at around +0.15V vs. SCE, which corresponds to Ni anodic etching in HNO_3 [14]. Two reduction peaks at -0.04V (D1) and at -0.12 V (D2) vs SCE, D1 and D2, can be seen, which in agreement with previous report [8] can be assigned to the formation of Bi_2Te_3 (D1) and elemental Bi deposition (D2) respectively. On the basis of the voltammetric studies stoichiometric films with a composition of Bi_2Te_3 could be reproducibly deposited over the potential range from 0V to -0.1V vs. SCE.

Electrodeposition is carried from electrolyte solutions containing a ratio of $[Bi^{3+}]/[Te^{4+}]= 1$ by pulsed electrodeposition employing zero current resting pulses for 2-5s and deposition pulses for 10-100 ms at -0.01 V to -0.06 V vs. SCE which were identified as the optimum electrodeposition conditions to grow thick layers of stoichiometric Bi_2Te_3 films at average film growth rates up to 50 μm/hour. Figure 2 shows a representative current and potential profile during pulsed electrodeposition of bismuth telluride. The pulse deposition at the beginning is critical, as very short pulses can create more nucleation sites on the Ni surface, and lower porosity and less preferred crystal orientation growth than continuous deposition [15, 16]. This improves the coverage of the Ni surface for subsequent deposition. The deposition current did not change much for the most part, until at the later stage it started to increase gradually, this is because the surface has become rougher and rougher as the thickness increased, and so the surface area has become bigger and bigger. This indicates that

a small piece of Bi_2Te_3 chip attached to Pt counter electrode can effectively replenish the depletion of bismuth and tellurium ions.

The deposited film thickness is pre-determined by the cathodic charge consumed in the deposition process assuming 100% current efficiency which is Q=1.66 coulomb/ μm/cm^2. The deposited film thickness was found to be around 95% of the calculated film thickness which is in line with that reported by other studies [10]. Due to the strong adhesion between bismuth telluride and the etched Ni, thicker than 500 μm film can be deposited on the pre-treated Ni substrate without cracking.

Representative topographical as well as cross-sectional SEM images in combination with EDX data of electrodeposited bismuth telluride films are presented in Figure 3. As the thickness increases, the surface of the deposit becomes slightly rougher as can be seen in Figure 3(a). However, the cross-sectional images reveal a compact film structure. Backscattering SEM images as shown in Figure 3(c) reveal a uniform element distribution across the film thickness, and the EDX analysis along the cross section shows nearly constant composition with an atomic ratio of Te/Bi=1.50, indicating a stoichiometric Bi_2Te_3 material. A small compositional deviation in the later stages of deposition can be seen. This might due to a decrease in the electrical conductivity of the deposited Bi_2Te_3 film on the Ni substrate as the film becomes very thick.

Figure 4 shows a typical XRD pattern recorded for pulsed electroposited Bi_2Te_3 films. All XRD peaks can be indexed to a rhombohedral Bi_2Te_3 crystal structure according to the standard ICDD PDF card (PDF-2/release 2012 RDB). A sharp peak corresponding to the (110) lattice plane can be observed indicating a preferential orientation in the (110) direction, corresponding to basal planes perpendicular to the substrate [8, 9] which coincides with the preferential orientation of films exhibiting the best thermoelectric performance. The average

grain size of the films is calculated to be 17.0 nm based on the Scherrer equation, which is much larger than previously reported grain sizes of 4.3 nm obtained by galvanostatic and potentionstatic deposition [17,18]. Hall effect measurements conducted on electrodeposited Bi_2Te_3 films showed that the films were n-type with an electrical conductivity of 330 S/cm carrier concentration of 10^{20} cm^{-3} and a mobility of 140 $cm^2/(V \cdot s)$ which is in agreement with literature values [10]. The average Seebeck coefficient was - 80μV/K which is also consistent with n-type conductivity. These data are in line with those reported for films of Bi_2Te_3 previously fabricated by electrodeposition [10] and other deposition methods such as MOCVD and MBE and the values obtained for the transport properties, carrier concentration and Hall mobility are also close to the optimum values that are required for thermoelectric applications [3].

CONCLUSIONS

Thick and uniform Bi_2Te_3 films were deposited on nickel substrates by electrochemical deposition from nitric acid solutions. Films with thicknesses of up to 800 μm were achieved over an area of 1 cm^2 resulting in uniform and compact stoichiometric Bi_2Te_3 films, which were found to be well adherent to the Ni substrate with excellent thermoelectric properties. The results obtained in this study pave the way for real TE device fabrication based on electrodeposited Bi_2Te_3 thick films.

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Figure 1. Cyclic voltammogram of 1cm^2 Ni working electrode immersed in 2M HNO_3 + 70mM $HTeO_2$ + 70m M Bi^{3+}, recorded at a scan rate of 20 mV/s.

Figure 2. Current and potential profile acquired during pulsed electrodeposition of bismuth telluride recorded at -30mV for 0.01s, 0A for 4s, on 1cm^2 Ni working electrode immersed in 2M HNO_3 + 70mM $HTeO_2$ + 70mM Bi^{3+}

Figure 3: 800 µm Bi_2Te_3 film deposited at pulsed -30mV vs. SCE from an electrolyte solution containing 2M HNO_3+70 mM $HTeO_2$+70mM Bi, (a) surface SEM image, (b) cross section SEM image, (c) cross section backscattering SEM image, (d) cross section composition corresponding to positions in (b).

Figure 4. XRD diffractogram of stoichiometric thick Bi_2Te_3 layer electrodeposited from 2M HNO_3, 70 mM $HTeO_2$ and 70mM Bi for 3h at 298 K.

FIGURES

Figure 1

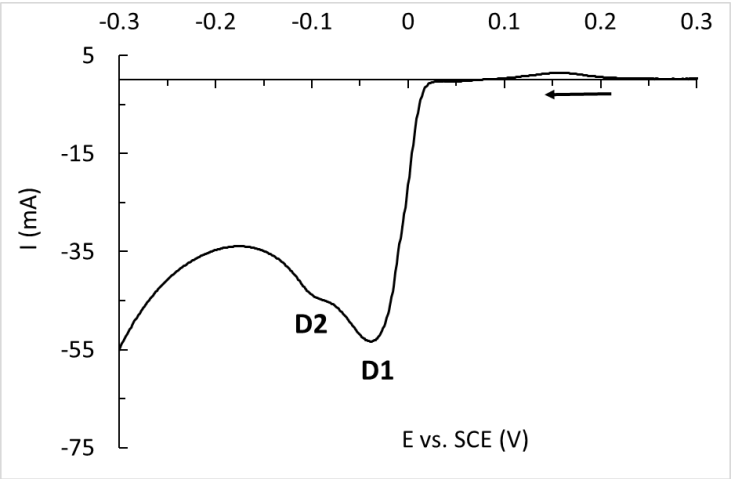

Figure 2

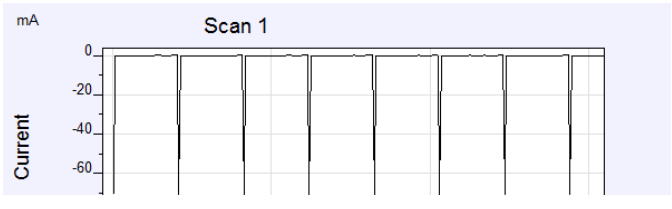

Figure 3

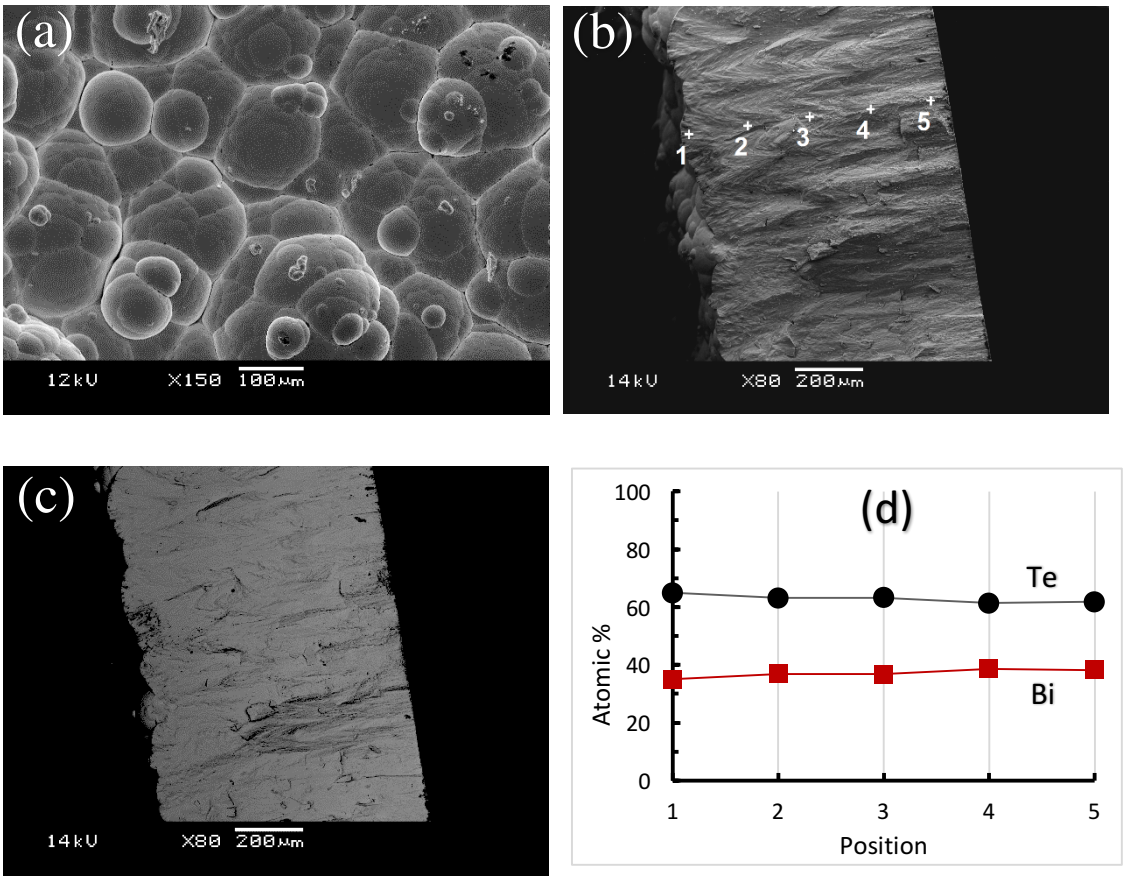

Figure 4