



Short communication

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 2 M nitric acid baths containing bismuth and tellurium dioxide on 1 cm^2 nickel (Ni) substrates at average film growth rates of $\sim 50 \mu\text{m}/\text{h}$. Pre-treatment of the Ni substrate was found to significantly enhance the adhesion of Bi_2Te_3 material onto Ni while 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 $-80 \mu\text{V}/\text{K}$ and an electrical conductivity of $\sim 330 \text{ S}/\text{cm}$ at room temperature.

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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 $\sim 10\%$ [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 ($\geq 300 \mu\text{m}$) [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 $> 500 \mu\text{m}$ was achieved.

In this report, we describe the optimized electrochemical deposition conditions that were employed to produce uniform and compact and well adherent Bi_2Te_3 layers on Ni with thicknesses $> 500 \mu\text{m}$ 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 $\text{M}\Omega \text{ cm}$. Bi powder (Alfa Aesar, 99.5%), Te powder (Alfa Aesar, 99+%), TeO_2 powder (Alfa Aesar, 99.99%), Ni foil (Alfa Aesar, 0.127 mm 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 $[\text{Bi}]/[\text{Te}] = 0.75\text{--}1.2$, dissolved in 2 M HNO_3 . The maximum concentration of TeO_2 that could be dissolved in 2 M HNO_3 was found to be $\sim 70 \text{ mM}$ even though a value of up to 80 mM was previously reported in the literature [8].

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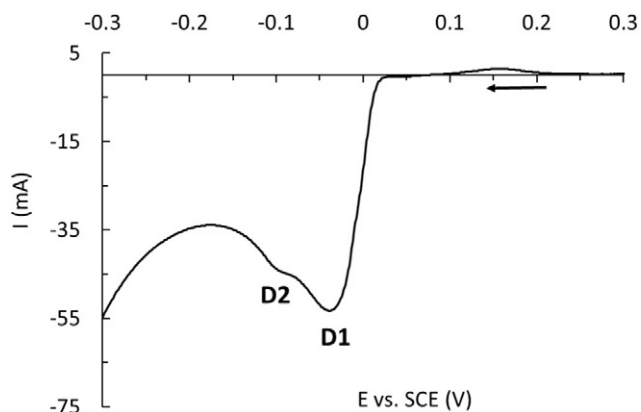


Fig. 1. Cyclic voltammogram of 1 cm² Ni working electrode immersed in 2 M HNO₃ + 70 mM HTeO₂ + 70 mM Bi³⁺, recorded at a scan rate of 20 mV/s.

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 Bi₂Te₃ as the counter electrode as reported in the paper [8], a small (~0.2 cm²) piece of a Bi₂Te₃ 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 1 cm² area. Prior to electrodeposition, Ni foil substrates are etched in concentrated HCl solution for 1 min, followed by anodic etching in 1 M HNO₃ at a potential of +0.15 V vs. SCE for 30 s. 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 2–5 s 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 were 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 K α radiation ($\lambda = 1.5406 \text{ \AA}$). 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. It should be noted that although the coatings are sufficiently well bonded to the substrate they could be mechanically processed in this manner. Commercial 0.2 mm 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 ($\mu\text{V/K}$) 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

Fig. 1 shows the representative cyclic voltammograms for bismuth telluride electrodeposition recorded at a 1 cm² Ni foil working electrode immersed in electrolyte solutions containing 2 M HNO₃ + 70 mM TeO₂ + 70 mM Bi³⁺ at a scan rate of 20 mV/s. The potential was swept from +0.5 V to –0.4 V versus a SCE reference electrode. A small oxidation peak appeared at around +0.15 V vs. SCE, which corresponds to Ni anodic etching in HNO₃ [14]. Two reduction peaks at –0.04 V (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 Bi₂Te₃ (D1) and elemental Bi deposition (D2) respectively. On the basis of the voltammetric studies stoichiometric films with a composition of Bi₂Te₃ could be reproducibly deposited over the potential range from 0 V to –0.1 V vs. SCE.

Electrodeposition is carried from electrolyte solutions containing a ratio of $[\text{Bi}^{3+}]/[\text{Te}^{4+}] = 1$ by pulsed electrodeposition employing zero

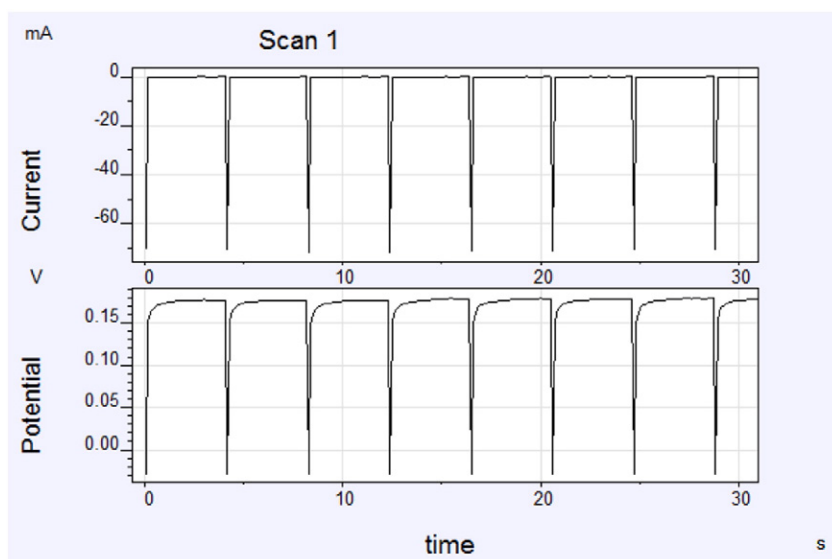


Fig. 2. Current and potential profile acquired during pulsed electrodeposition of bismuth telluride recorded at –30 mV for 0.01 s and 0 A for 4 s, on 1 cm² Ni working electrode immersed in 2 M HNO₃ + 70 mM HTeO₂ + 70 mM Bi³⁺.

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