This is an author produced version of a paper published in:

Electrochemistry Communications

Cronfa URL for this paper:
http://cronfa.swan.ac.uk/Record/cronfa50241

Paper:
http://dx.doi.org/10.1016/j.elecom.2016.02.005

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

http://www.swansea.ac.uk/library/researchsupport/ris-support/
Electrochemical deposition of Bismuth Telluride

Thick layers onto Nickel

C.Lei‡, K.S. Ryder†, E. Kouharenko‡, M. Burton‡ and Iris S. Nandhakumar,*‡

‡School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK. Fax: 02380 59378; Tel: +44 23806877; E-mail: iris@soton.ac.uk
†Materials Centre, Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK.

KEYWORDS: Bismuth telluride, electrodeposition, thick films

Abstract

Bismuth telluride (Bi$_2$Te$_3$) 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$_2$Te$_3$ 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$_2$Te$_3$ 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$_2$Te$_3$ 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$_2$Te$_3$) 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 \( \text{Bi}_2\text{Te}_3 \) films are required as thick layers for practical TE devices (\( \geq 300 \) \( \mu \)m) [5-7]. However, to obtain uniformly thick \( \text{Bi}_2\text{Te}_3 \) films by electrodeposition still represents a significant challenge due to a number of factors: the \( \text{Bi}_2\text{Te}_3 \) 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 \( \text{Bi}_2\text{Te}_3 \) thick films a number of strategies have been employed which include the use of pulsed electrodeposition [8] and the use of a soluble \( \text{Bi}_2\text{Te}_3 \) anode [9].

There is considerable interest to deposit \( \text{Bi}_2\text{Te}_3 \) 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 \( \text{Bi}_2\text{Te}_3 \) legs [3]. Electrodeposition of \( \text{Bi}_2\text{Te}_3 \) 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 \( \text{Bi}_2\text{Te}_3 \) onto Ni [12, 13] and this study represents the first study in which extremely thick layer deposition >500 \( \mu \)m was achieved.
In this report, we describe the optimised electrochemical deposition conditions that were employed to produce uniform and compact and well adherent Bi₂Te₃ 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+%), TeO₂ powder (Alfa Aesar, 99.99%), Ni foil (Alfa Aesar, 0.127mm thick, 99+) and HNO₃ (Fisher, 70%) were used as received. The electrolyte solution consists of 70 mM TeO₂ and Bi with a ratio of [Bi]/[Te]=0.75-1.2, dissolved in 2M HNO₃. The maximum concentration of TeO₂ that could be dissolved in 2M HNO₃ 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 Bi₂Te₃ as the counter electrode as reported in paper [8], a small (~0.2cm²) 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 1cm² area. Prior to electrodeposition, Ni foil substrates are etched in concentrated HCl solution for 1min, followed by anodic etching in 1M HNO₃ 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 (λ = 1.5406Å).

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$_2$Te$_3$ (D1) and elemental Bi deposition (D2) respectively. On the basis of the voltammetric studies stoichiometric films with a composition of Bi$_2$Te$_3$ 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 versus SCE which were identified as the optimum electrodeposition conditions to grow thick layers of stoichiometric Bi$_2$Te$_3$ 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$_2$Te$_3$ 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 \( Q = 1.66 \text{ coulomb/} \mu \text{m/cm}^2 \). 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 \( \mu \text{m} \) 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$_2$Te$_3$ 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$_2$Te$_3$ film on the Ni substrate as the film becomes very thick.

Figure 4 shows a typical XRD pattern recorded for pulsed electroposited Bi$_2$Te$_3$ films. All XRD peaks can be indexed to a rhombohedral Bi$_2$Te$_3$ 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$_2$Te$_3$ 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·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$_2$Te$_3$ 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$_2$Te$_3$ 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$_2$Te$_3$ 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$_2$Te$_3$ thick films.

REFERENCES


ACKNOWLEDGEMENTS
We are grateful to Innovate UK for the award of a TSB grant (TS/L008157/1) and to European Thermodynamics and Scionix for their support throughout this project. We acknowledge the financial support of equipment grant (EP/K00509X/1) for the SmartLab.

**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$_2$Te$_3$ 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$_2$Te$_3$ layer electrodeposited from 2M HNO$_3$, 70 mM HTeO$_2$ and 70mM Bi for 3h at 298 K.

FIGURES

Figure 1

![Figure 1](image1)

Figure 2

![Figure 2](image2)
Figure 3

(a) 

(b) 

(c) 

(d) 

Figure 4