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A novel route to nanostructured bismuth telluride films by electrodeposition

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A B S T R A C T

We report a novel route to the fabrication of 3D nanostructured stoichiometric bismuth telluride (Bi_2Te_3) films by electrodeposition through inverse lipid cubic phases as evidenced by Small-angle X-ray Scattering (SAXS) and Helium Ion Microscopy (HIM). The nanostructured Bi_2Te_3 films were composed of interconnected nanowires with diameters of 60–150 Å.

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1. Introduction

Thermoelectric (TE) materials are an important class of materials that can directly convert thermal waste heat into useful electrical energy using the Seebeck effect [1]. The currently best performing TE materials in commercial TE devices are based on bulk Bi_2Te_3 used for refrigeration and waste heat recovery up to 200 °C [2]. Theoretical calculations by Dresselhaus et al. [3,4] predict that low dimensional structures such as 1D nanowires or 2D quantum wells systems could dramatically enhance the thermoelectric performance of materials due to quantum confinement effects and enhanced phonon scattering at heterointerfaces that leads to a reduction in the thermal conductivity. This has stimulated considerable interest in the synthesis of Bi_2Te_3 nanowires. One widely used approach for producing nanowires of Bi_2Te_3 involves deposition (either chemically or electrochemically) into porous anodically etched alumina templates with the smallest electrodeposited nanowires reaching diameters down to 150 Å [5]. Alumina however has a high thermal conductivity of 1.9 WmK^{-1} [6] which makes TE characterization of the embedded nanowires extremely difficult due to parasitic heat transfer whilst removal of the alumina template requires harsh chemical conditions [7]. Alternatively polymeric membranes with low thermal conductivities (e.g. 0.21 W mK^{-1} for polycarbonate) have also been employed as nanotemplates for bismuth telluride nanowire growth [8–11]. Polycarbonate templates can be removed with solvents such as dichloromethane or dimethylformamide, however freestanding nanowires with an aspect ratio of 10 or higher will collapse [7]. Zhang and co-workers [12] have reported a non-templated solvo-thermal route to ultrathin Bi_2Te_3 nanowires with average diameters of 80 Å. This requires temperatures of 160 °C to produce the separate nanowires; they are then spark plasma sintered at several hundred °C and 50 MPa axial pressure to consolidate the wires into a continuous electrical contact. In contrast, in this manuscript we describe an electrochemical route to a network of ultrathin Bi_2Te_3 nanowires with comparable diameters using a 3D cubic lipid phase template. The deposition occurs at room temperature; and the 3D connected end product and the fact that the electrochemical route produces a material already connected to the electrode surface remove the need for a sintering step. This makes our method potentially attractive for use with electrode substrates which either have complex geometries or contain materials not compatible with the high temperatures associated with the sintering processes used by Zhang et al. [12]. In this paper, for example, we describe the deposition of Bi_2Te_3 nanowires onto electrodes formed from archival DVDs comprising a layer of gold on a backing of polycarbonate, which softens at 145 °C [13], and which therefore require relatively mild deposition conditions.

3D cubic lipid phases offer a promising synthetic route to the production of nanowires with diameters < 10 nm as illustrated for freestanding nanowire networks of platinum [14,15]. We hypothesise that the application of these templates instead to thermoelectric

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semiconductors would open up the possibility of producing nanowires with ultralow diameters for efficient thermoelectric generators [1] that would potentially exhibit an increased Seebeck coefficient due to quantum confinement on the electron density of states [3,4]. Nanowire networks that are composed of highly interconnected nanowires are mechanically stable and can be more easily manipulated and fabricated into devices and potentially exhibit significantly higher thermoelectric performance as predicted by theoretical studies due to a reduction in thermal conductivity via branching [16].

We herein report a novel route to the fabrication of 3D nanostructured bismuth telluride films that are composed of 60–150 Å interconnected nanowires. This approach utilises Type II inverse bicontinuous cubic phases $(Q_{II})^D$ of the lipid phytantriol as templates for electrodeposition. Type II lyotropic liquid crystal systems (LLC) are characterized by an interface that curves towards water and includes the inverse hexagonal phase (H_{II}), containing water cylinders, and the inverse bicontinuous cubic phases (Q_{II}), which contain a single lipid bilayer on either side of which lie branching networks of nanometre-sized water channels. There are 3 inverse bicontinuous cubic phases which can form: the 'primitive' (Q_{II}^P), 'double diamond' (Q_{II}^D), and 'gyroid' (Q_{II}^G). The lipid phytantriol forms the Q_{II}^D phase in excess water which was used as the template in this work.

2. Experimental

All chemicals were used as received. Phytantriol (3,7,11,15-tetramethyl-1,2,3-hexadecanetriol) was purchased from Adina Cosmetics, Bi powder (99.999%) was purchased from Alfa-Aesar, TeO_2 (99.9995%) was purchased from Sigma-Aldrich, nitric acid (70% laboratory grade) was purchased from Fisher, deionized water was purified by a Milli-Q system to 18.2 MΩ cm and ethanol (laboratory grade) was purchased from Fisher. 10 mM TeO_2 and 1 M HNO_3 electrolytes with Bi^{3+} concentrations varying from 7.5 mM to 17 mM were produced by adding 3.125 mL of nitric acid (70% laboratory grade) to 0.0798 g of TeO_2 and between 0.0784 g and 0.1776 g of Bi. This was left stirring for 12 h, or until dissolved. Deionized water was then used to make up to a 50 mL solution. This was purged with nitrogen for no less than 20 min to remove dissolved oxygen.

Nanostructured bismuth telluride films were prepared by potentiostatic electrodeposition from an electrolyte containing 17 mM Bi and 10 mM TeO_2 in 1 M HNO_3 through phytantriol modified gold electrodes. The lipid template was applied by dip coating into a solution of ethanol and phytantriol 1:2(*w*/w). Once dip coated the substrate was left for no less than 30 min to allow the ethanol to evaporate, leaving an estimated 22 ± 1 μm thin film of phytantriol coating[14]. The substrate could then be immersed into the electrolyte and left to equilibrate for no less than 30 min prior to deposition. Deposition was carried out on Au archival DVDs (Belkin), for SAXS; Au on Si wafers (p-type (100) Si wafers with 20 nm of Ti sputtered, followed by 200 nm Au sputtered on top), for Helium Ion Microscopy (HIM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Seebeck characterizations. Au on Si wafers were sonicated in isopropyl alcohol (IPA) for 10 min then washed with deionized water immediately prior to use. The plastic layers of the Au DVDs were separated immediately prior to use. For all substrates, polyimide tape was used to define a working electrode area of 1 cm^2 and Cu tape was used to make contact to the working electrodes. Electrodeposition was carried out using a conventional three electrode configuration. The reference electrode was a saturated calomel electrode (SCE). A Pt mesh was used as a counter electrode, which was flame annealed prior to use to remove any contaminants. After deposition samples were rinsed in deionized water before being submerged in ethanol for 30 min to remove the template.

SAXS measurements were carried out at Diamond light source on beamlines; I07 with beam energy and size of 13.0 KeV and 150 μm × 80 μm respectively and I22 with beam energy and size of 12.4 KeV and 320 μm × 80 μm respectively. Pilatus 2 M detectors were used on both beamlines to collect data over the q range of $0.05\ Å^{-1}$–$0.30\ Å^{-1}$. Calibration was achieved by using a silver behenate sample. Phases were indexed by assigning Bragg peaks to known phases. SEM images were taken on a Zeiss EVO LS25 ESEM microscope and EDX taken using an Oxford Labs attachment for compositional analysis. HIM images were taken on a Zeiss Orion Helium Ion Microscope. XRD patterns were obtained using a Rigaku SmartLab diffractometer using CuKα radiation. Seebeck coefficients were measured by a custom-made Seebeck measurement unit that was calibrated against a polycrystalline Bi foil reference standard.

3. Results and discussion

Electrochemical deposition through a thin layer of self-assembled double-diamond phase (Q_{224}) of phytantriol was performed over a wide deposition potential window of −0.375 V to −0.05 V vs SCE and electrolyte bath compositions in order to identify the optimum electrodeposition parameter for generating stoichiometric films as this directly influences their thermoelectric properties. EDX analysis as shown in Fig. 1 revealed that stoichiometric Bi_2Te_3 films could be prepared from electrolyte solutions composed of 10 mM TeO_2 and

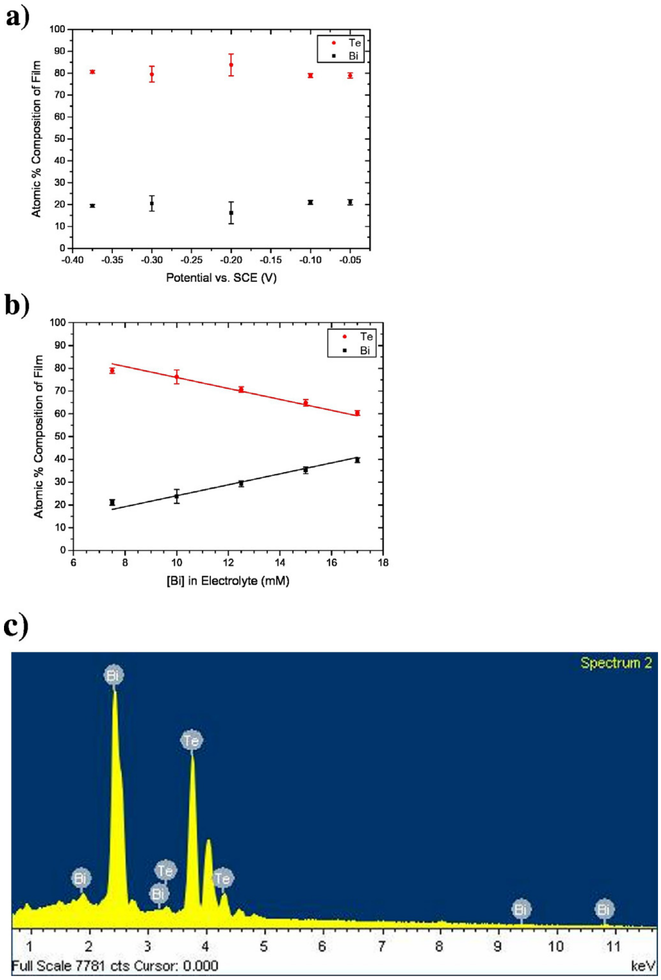

Fig. 1. EDX of electrodeposited thin films of bismuth telluride. a): deposited from an electrolyte composed of 7.5 mM Bi, 10 mM TeO_2 and 1 M HNO_3, at potentials of −0.375, −0.30, −0.20, −0.10 and −0.05 V vs SCE, b): deposited from an electrolyte of 10 mM TeO_2, and 7.5, 10.0, 12.5, 15.0 or 17.0 mM Bi dissolved in 1 M HNO_3 at a potential of −0.05 V vs SCE. Deposition was through phytantriol for a time of 2 h. The linear fits are fixed to intercept at 0% and 100% for Bi and Te respectively. Error bars donate the 95% confidence limits. c) EDX trace of electrodeposited bismuth telluride film showing the presence of both bismuth and tellurium in the deposits.

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