ICT-ENERGY LETTERS

Thermoelectric characterization of electrochemically deposited Bismuth Telluride materials by microfabricated resistive thermometry

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***Abstract* - The present study is focused on the investigation of the thermoelectric properties of electrochemically deposited copper doped bismuth telluride selenide thin films. Such approach has the potential for reducing the cost of large scale manufacture of thermoelectric generators. A microfabricated fully integrated measurement device structure [1] has been adopted, enabling cross-plane electrical conductivity, thermal conductivity and Seebeck coefficient to be accurately determined on the same specimen. The characterization device includes integrated heater, thermometers and electrically contact plates at both the top and the bottom of the layer structure.**

I. INTRODUCTION

CONCERNS over increasing energy costs and global warming associated with fossil fuel is encouraging the search for cleaner and more sustainable energy sources. Among feasible technologies, particular attention has been directed to thermoelectric (TE) energy generators. These solid-state devices can improve the efficiency of a system by harvesting waste thermal energy and partially converting it into electricity. The main advantages of thermoelectric energy generators include: solid-state operation, zero-emissions, scalability, no maintenance and long operating lifetime.

The best commercially available TE materials for room temperature operation are bismuth telluride (Bi-Te) compounds. However, since Tellurium is the 9th rarest element on earth, it results suitable only for niche applications such as powering sensors, laboratory equipment and medical applications.

Theoretical studies have predicted that low-dimensional structures [2] and enhanced microstructural properties [3] could yield improved TE performance. Above all, preferential crystalline orientation in the (1 1 0) plane, due to strong anisotropy in physical properties, and optimized crystallite size are crucial for high-quality Bi-Te materials [4].

Electrochemical synthesis has been shown to provide a cost effective and scalable method to grow high-quality bismuth telluride compounds at room temperature, offering good control over composition and cristallinity.

The maximum efficiency of a thermoelectric material is determined by its figure of merit (*zT*):

$$zT = \frac{\alpha^2 \sigma T}{k} \qquad (1)$$

in which α is the Seebeck coefficient, σ and κ are respectively electrical and thermal conductivity, and *T* is the temperature.

A second figure of merit, the power factor, which quantifies the ability of a material to produce useful power output while under a given temperature difference, is instead defined as:

$$\alpha^2 \sigma \qquad (2).$$

Therefore, electrical and thermal properties of interest, as well as their coupling, appear clear. However, the ability to measure many properties becomes less and less feasible at the nanoscale limit.

The access to the James Watt Nanofabrication Centre (JWNC) offered the opportunity to design and fabricate a characterization structure through which do probe TE parameters directly on the bismuth telluride thin film.

Indeed, whilst there have been a significant number of publications investigating electrical conductivity [5] and power factor of Bi-Te thin films [6], to date none has achieved simultaneous measurements of thermoelectric properties. In this paper, we present the fabrication of a characterization pillar structure with integrated heater, thermometers and electrical probes to allow electrical conductivity, thermal conductivity and Seebeck coefficient to be extracted from a single device. A brief notice concerning preliminary measurement is also included.

II. MATERIAL

SOI (Silicon On Insulator) substrates are coated with a 200 nm thick electron beam evaporated gold layer and then used as electrodes for the electrochemical deposition. From Bi and TeO_2 electrolytes, in nitric acid baths at an applied potential of about +0.05 V, the growth achieves around 7 μm thick copper doped $Bi_2Te_{2.7}Se_{0.3}$ films with (1 1 0) preferred crystallite orientation. Deposition and crystallography analysis (Energy-Dispersive X-ray, EDX, and X-Ray Diffraction, XRD) are performed at the School of Chemistry of the University of Southampton [4].

III. DEVICE FABRICATION

As previously mentioned, due to the coupling of the thermoelectric parameters, it is preferable to measure the electrical and thermal properties of the material on a single device.

Previous work has demonstrated a test structured based on the Van Der Pauw geometry [7], which would however be inapplicabile to electrochemically grown thin films, as their bottom is short-circuited by the metal layer adopted as electrode for the deposition. Therefore, a vertical heat flow characterization structure has been designed, Fig. 1, and fabricated, Fig. 2.

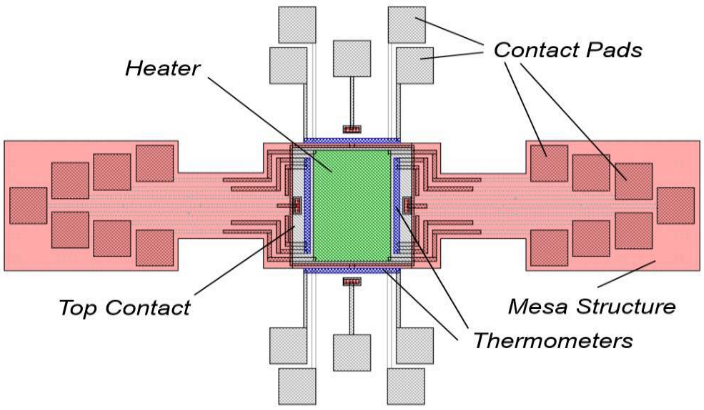

Fig. 1. L-Edit design of the fully integrated structure (top view).

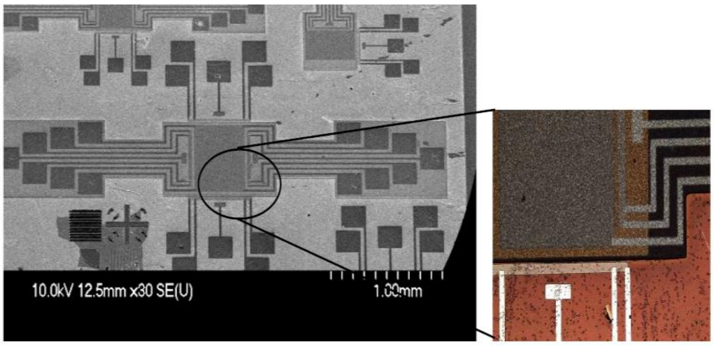

Fig. 2. SEM (Scanning Electron Microscope) top view image of the fabricated device together with an optical microscope image illustrating a detail of the structure.

The sample initially undergoes a Chemical Mechanical Polishing (CMP), which brushes the top surface of the thin film reducing its superficial roughness, as shown in Fig. 3. Atomic Force Microscopy (AFM) analysis demonstrates a roughness reduction from about 100 nm rms (500 nm peak to peak value) before the polishing to 2 nm rms (20 nm peak to peak value) after. The polishing is immediately followed by an ammonium peroxide clean and a subsequent water rinse, which dissolve the residual particles of brushing slurry off the sample.

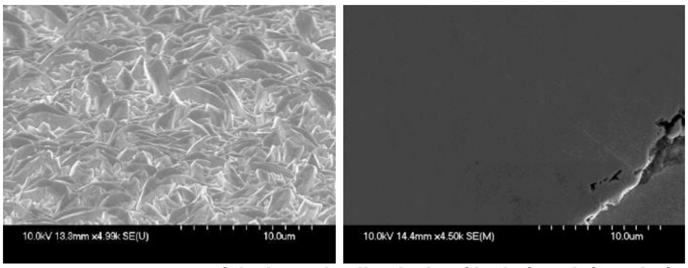

Fig. 3. SEM top view of the bismuth telluride thin film before (left) and after (right) processing the CMP.

The device mesa structure is then realized by inductively coupled plasma (ICP) etch recipe mixing O_2, CH_4 and H_2. The process adopts a 300 nm thick ICP deposited Si_3N_4 mask patterned by i-line photolitography and reactive ion etching (RIE). At a later stage, the Si_3N_4 mask is removed by RIE and the oxide layer covering the thin film is wet etched in a 10% HNO_3 solution.

Metallic (50 nm Ni, 10 nm Pt, 100 nm Au) contacts are patterned on top of the test structure by photolitography, metal evaporation and lift-off. The whole sample is coated by 100 nm ICP deposited Si_3N_4 which realizes electrical and thermal passivation.

Finally, after opening windows in the passivation layer by RIE etching, thermometers (100 nm Pd), heaters (50 nm NiCr) and contact pads (300 nm Al) are patterned by photolithograpy and metal lift-off.

IV. PRELIMINARY MEASUREMENTS

The copper doping increases the expectation for improved Seebeck coefficient and electrical and thermal properites which yielded to a power factor of 59.9 ± 12.5 mW $m^{-1}K^{-2}$. Furthermore, preliminary measurements already presented higher Seebeck coefficient compared to continuosly deposited films.

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