TOWARDS NANOSTRUCTURED THERMOELECTRIC GENERATOR FOR ENERGY HARVESTING

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Abstract: This paper presents the development processes towards a new generation of nanostructured thermoelectric generators for power harvesting from small temperature gradients by using a combination of traditional silicon microfabrication techniques, electroplating and submicron ion-track nanolithography. Polyimide nanotemplates with pore diameters ranging from 30nm to 120 nm were fabricated. Preliminary results for Bi_2Te_3 nanowires (50 and 120 nm diameter) electroplated into polycarbonate ion-track commercial membranes are presented. Bi_2Te_3 nanowires of R^-3m structure, with preferential orientation in the (015) and (110) crystallographic plans with nearly stoichiometric composition were electroplated. The fine-grained observed microstructure (6-10 nm) and (110) crystalline orientation appear extremely promising for improving thermoelectric material properties.

Key Words: thermoelectric generator, nanostructure, ion-track, polyimide

1. INTRODUCTION

The rapid increase in the development of remote wireless devices, embedded structures and portable electronics demonstrates the need for self-sufficient local power sources. The powering of wireless devices from energy harvested from the environment (e.g. solar, wind, vibration and thermoelectric) presents an alternative to batteries, which are bulky and contain a finite amount of energy. Thermoelectric power generation presents many advantages including solid-state operation with no moving parts, long life (~ 20 years), and high reliability [1]. The drawbacks of existing thermoelectric generators are low efficiency and large size (~3500mm^3) [2]. This paper presents the development of a new generation of nanostructured thermoelectric generators for power harvesting from small temperature gradients by using the combination of traditional silicon microfabrication techniques and submicron ion-track processes.

The efficiency of thermoelectric (TE) materials is determined using the figure of merit $ZT=(\alpha^2T/\rho K_T)$, where α, T, ρ and K_T are the Seebeck coefficient, absolute temperature, electrical resistivity and thermal conductivity respectively [1]. The best TE materials commercially available today have a ZT of ~ 0.9. Nanostructured materials have recently attracted great interest because theoretical studies have predicted that efficiency is increased by a factor of ~3 if the thermoelectric element's 'leg' diameter can be decreased to a size at which quantum confinement and interface scattering effects occur [3]. Currently, there are different techniques to miniaturise thermoelectric devices using micro/nano-templates from Al or microphotolithography. These methods have limitations in size, density of thermoelectric elements, complexity and high cost. The current state-of-the-art of a micro-thermoelectric $Bi_{2-x}Sb_xTe_3$ device presented by G. Jeffrey has TE elements of 20µm length and 60µm in diameter, and generates a maximum power of ~ 1 µW which is not sufficient for most of today's wireless sensor applications [4].

In this work, a substantial improvement in efficiency (ZT>>2) will be achieved by using Bi-Sb-Te nanowires fabricated by electroplating into nanotemplates prepared by ion-track irradiation. A schematic view of the thermoelectric micro generator is shown in Fig. 1. Ion-track technology can produce low-cost templates for nanowires with a diameter < 50nm with and very-high-aspect-ratio structures (more than 1000) [5]. This technique uses accelerated heavy ions as a source to modify the template material, making it

susceptible to chemical etching in the direction defined by the irradiation.

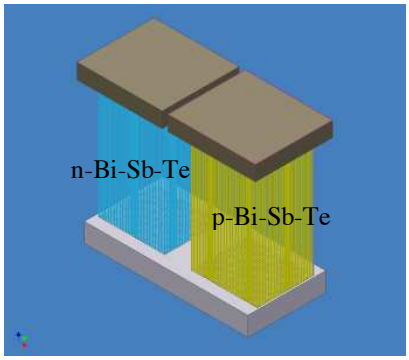

Fig. 1: Schematic view of the TE device.

2. EXPERIMENTAL

2.1 Nanotemplates etching

We have studied track etching in polyimide (PI2731 wet type photoresists from HD Microsystems and also dry films of Kapton HN from Dupont of 12.7 µm thick) onto silicon substrates with and without a gold seed layer, irradiated with Pb projectiles of ~2.3 GeV kinetic energy. Samples irradiated with $5x10^8$ ions/cm^2 and $5x10^9$ ions/cm^2 were pre-etched in H_2O_2 solution at 60°C or 90°C and subsequently etched in sodium hypochlorite (NaClO, (13%, pH~12.6) solution at 60°C. The resulting pores were observed using scanning electron microscopy (SEM) (Fig. 2, Fig. 3, Fig. 4). Depending on the nature of etched polyimide (wet or dry type), etching time, temperature of the solutions (H_2O_2, NaOCl), and pH of NaOCl, the pore diameter varied between 30nm to 120nm for different samples of polyimide.

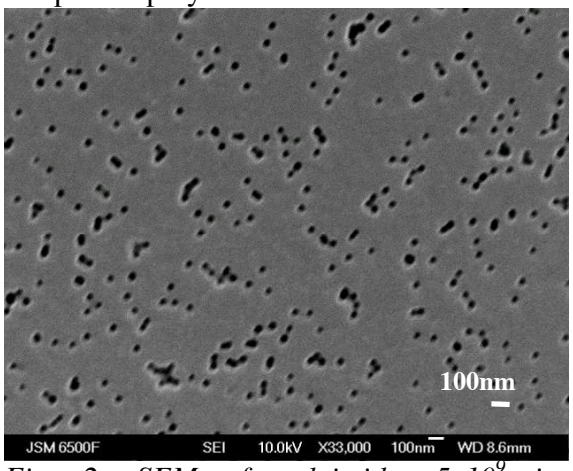

Fig. 2: SEM of polyimide, $5x10^9$ ions/cm^2 (PI2731, 10 µm thick), ion-track etched, 40min in H_2O_2 (60°C) followed by 5 min in NaOCl (60°C). Pores diameter from 30 to 50 nm.

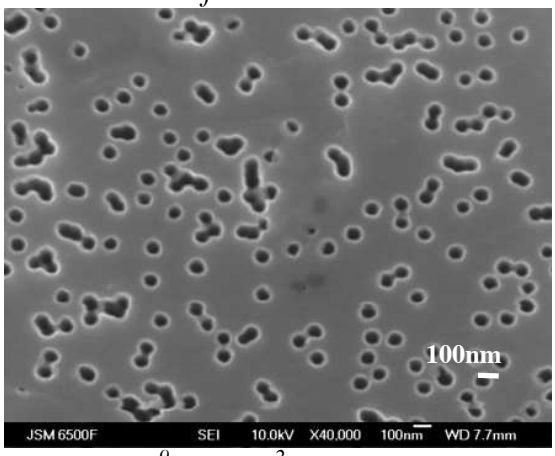

Fig .3: $5x10^9$ ions/cm^2 (Kapton, 12.7 µm thick), ion-track etched, 40min in H_2O_2 (60°C) followed by 5 min in NaOCl (60°C). Pores diameter from 40 to 70 nm.

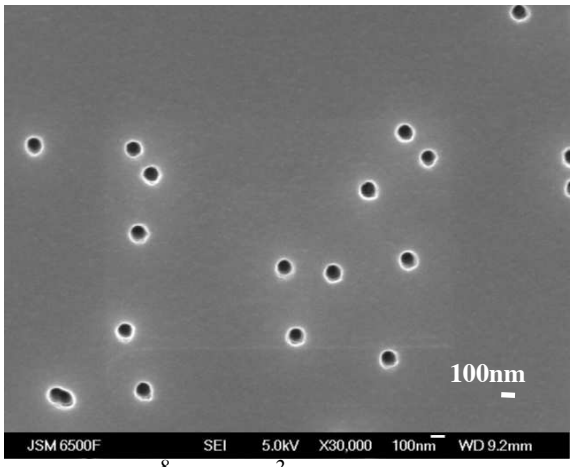

Fig .4: $5x10^8$ ions/cm^2 (Kapton, 12.7 µm thick), ion-track etched, 40min in H_2O_2 (90°C) followed by 5 min in NaOCl (60°C). Pores diameter from 100nm to 120 nm.

Typically, the smallest pore sizes of 30-50 nm were observed for PI2731, wet type polyimide. In all cases there was a poor adhesion between polyimide layer and Au-seed layer substrate.

2.2 Bi-Te nanowires electroplating

As a preliminary study, Bi_2Te_3 nanowires were electroplated into the template of commercial ion-track polycarbonate membrane from Millipore of ~ 6µm thickness with pores diameters of ~ 120 nm.

Electroplating was carried out by cathodic electrochemical codeposition of bismuth and tellurium powder dissolved in the aqueous nitric acid using a three-electrode cell with an Autolab potentiostat/galvanostat. It was found that the

electrodeposition conditions (such as e.g. current density, deposition potential and temperature) have a significant effect on the Bi_2Te_3 nanostructure and morphology. The samples were electrodeposited in the plating bath at room temperature. For a broad range of applied potentials, from -0.22 V to 0.03 V vs a Saturated Calomel Electrode (SCE), the resulting Bi_2Te_3 compounds show a stoichiometric composition. Fig. 5 presents preliminary results for Bi_2Te_3 nanowires electroplated into polycarbonate nanotemplates. It can be seen that the average diameter of the nanowires is about 120 nm, which is consistent with the pore size of the polycarbonate membrane.

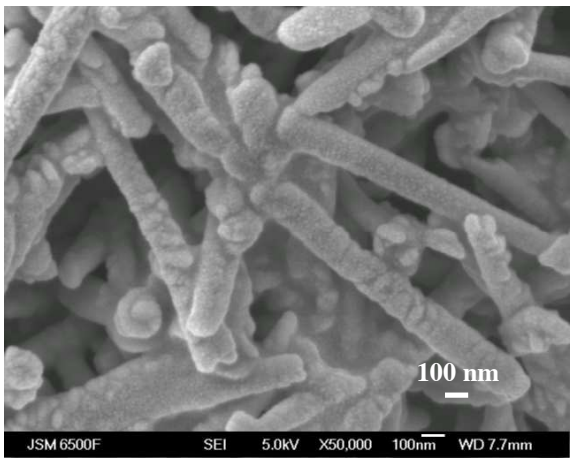

Fig 5: SEM image of Bi_2Te_3 nanowires deposited at –0.2 V vs SCE at room temperature from polycarbonate membrane with a pore diameter of 120 nm.

2.3 Bi-Te nanowires microstructural characterization

The surface morphology and compositions of the Bi_2Te_3 films and nanowires were characterized using a JSM-6500F scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) microanalysis (Oxford Inca 300) and operated at 20 kV. The crystal structures of Bi_2Te_3 films and nanowires were investigated using a Siemens D5000 X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å) and a transmission electron microscopy (TEM) (JEOL 3100 300 kV accelerating voltage).

Wide-angle X-ray Diffraction Spectroscopy (XRD) spectra revealed that the deposited nanowires have a rhombohedral structure, R^-3m (Fig. 6). The standard ICDD PDF card (82-0358) has been used to identify and index all detected peaks as those from Bi_2Te_3 crystal with space group R^-3m except for the peaks of Au, which come from the gold seed layer that was used as a working electrode.

A constant Te content of ~ 54 atom% (Fig.6) was determined by energy-dispersive X-ray spectrometry (EDX).

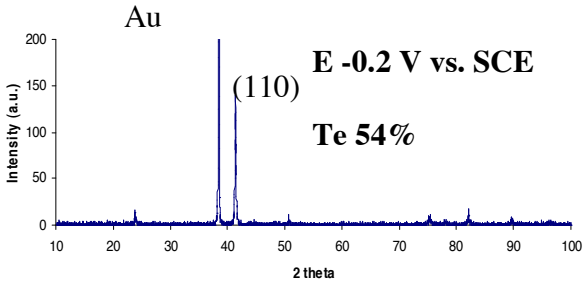

Fig. 6: XRD of Bi_2Te_3 nanowire composition by electroplating

Fig. 7 shows typical TEM images of the Bi_2Te_3 nanowires. It can be seen that the nanowires are uniform, continuous, and have diameters of 50 nm (Fig. 7a) and 120 nm (Fig. 7b), which correspond to the diameter of the polycarbonate templates. The selected area electron diffraction (SAED) pattern taken from the single nanowire (insert of Fig. 7b) indicates that the Bi_2Te_3 nanowire has a rhombohedral lattice structure and belongs to a space group R^-3m. This observation is in good agreement with XRD result.

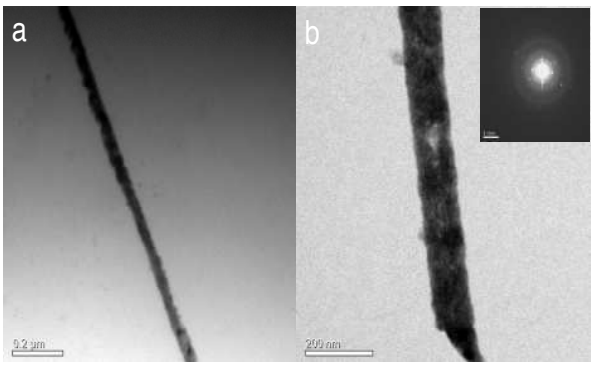

Fig. 7: TEM images of Bi_2Te_3 nanowires deposited at –0.2 V vs SCE at room temperature from polycarbonate membranes with different diameters (a) 50 nm and (b) 120 nm (inset is the selected area electron diffraction).

3. DISCUSSION

Our investigations on electrochemically deposited wires reveal that the crystallinity and texture can be controlled by the deposition parameters. Wires grown potentiostatically are (110) textured and agree with the results reported by Chaouni et al. [6]. Scanning electron microscopy (SEM) associated with energy-dispersive spectrometry, X-ray diffraction, and transmission electron microscopy (TEM) evidenced a microcrystalline structure with a single phase of Bi_2Te_3 with a composition close to stoichiometric and a preferential crystalline orientation in (110) plans. The fine-grained observed microstructure of 6-10 nm is promising for enhanced thermoelectric material properties, by way of reducing the thermal conductivity.

4. CONCLUSION

Polyimides have been shown to be promising materials for ion-track nanotemplates for use in electroplated Bi-Sb-Te nanowires. Such devices can be used for applications in thermoelectric nanostructured generators integrated with silicon microfabrication processes. Polyimide nanotemplates with 30-120nm pore diameters were fabricated. Preliminary Bi-Sb-Te electroplating of nanowires (50 and 120 nm diameter) was carried out with commercial ion-track polycarbonates. Bi_2Te_3 of R3d structure with close to stoichiometric composition has been deposited with the grain preferential orientation in (110) and fine grain size (6-10 nm) for optimal thermoelectric properties

Further improvements of the adhesion between the polyimide and Au-seed layer are currently being investigated.
The etching parameters of ion-track irradiated polyimides require further optimisation to ensure that etching occurs through the entire thickness of the film.

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