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Thermal Characterization of Nanowire Array in a-Al_2O_3 Matrix

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ABSTRACT

Thermal properties characterization of Bi nanowires is critical in order to validate the predicted enhancement of their thermoelectric figure-of-merit. In this paper we report the effective thermal diffusivity of Bi nanowires array embedded in a-Al_2O_3 (alumina) template. The composite material consists of 85% alumina and approximately 15% Bi nanowires with a diameter of 40 nm and an average length of 40 μm. Measurements are performed along the nanowire axis. A thermal wave is produced at the front side of the sample and it is monitored at the backside through a fast thermoelectric effect. A one-dimensional heat conduction model is used to extract the thermal diffusivity.

INTRODUCTION

The efficiency of a thermoelectric device is limited by the thermoelectric figure-of-merit of the material $Z = \sigma S^2/k$, where S is the Seebeck coefficient, σ is electrical conductivity, and k is the thermal conductivity. Currently, the best commercially available thermoelectric material $(BiSb)_2Te_3$ has a ZT of ~1, however thermoelectric devices based on this material cannot compete in performance with other well-established technologies.

Several approaches have been explored to increase the thermoelectric figure-of-merit [1,2]. Among those, low-dimensional thermoelectric materials structures such as quantum wells, superlattices and nanowires have been extensively investigated [3-7]. As predicted by Hicks and Dresselhaus [2,8], quantum effects in low-dimensional systems may result in increased density of states near Fermi level and consequently increased electrical conductivity and Seebeck coefficient. Furthermore, increased scattering of heat carriers from interfaces leads to a decreased thermal conductivity in such systems. In light of these, theoretical studies done on bismuth nanowires estimate a significantly enhanced thermoelectric figure-of-merit [5]. However, experimental measurements must be carried out in order to validate the theoretical estimations. While electrical properties and Seebeck coefficient of bismuth nanowires have been characterized [9], another key property of a material candidate to thermoelectric applications, thermal conductivity, has yet to be determined experimentally. However, manipulation and preparation of test specimens of nanometer size is not an easy task. Therefore, a first approach in

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exploring thermal properties of nanowires is to characterize them embedded in another media with known thermal properties

In this paper we report thermal diffusivity measurements of Bi nanowires in amorphous Al_2O_3 matrix. The composite material has 85% alumina and approximately 15% Bi nanowires. The nanowires are highly ordered, with a diameter of 40 nm and an average length of 40 μm. Thermal diffusivity measurement is carried out in the direction along the nanowire axis. Modulated heating is applied to the front side of the sample and the amplitude and phase of the temperature signal is monitored at the backside by a fast responding thermocouple. The thermal diffusivity is extracted by fitting the experimental data to a one-dimensional heat transport model. Preliminary results suggest that thermal diffusivity of the composite material is $1.3x10^{-6}m^2s^{-1}$. In order to extract the thermal diffusivity of Bi nanowires further investigation of thermal properties of the host alumina template must be carried out.

SAMPLE PREPARATION

The template used for the preparation of Bi nanowires is an anodic porous alumina, with highly ordered nanochannels formed by the anodization of aluminum. Thermal characterization was initially performed on commercially available templates (Whatman, Anodisc). However, SEM micrographs (Fig. 1(a)) of Whatman templates have shown that templates are not uniform and they have variable diameter across the thickness. Uniform pore size is critical in order to obtain consistent quantum effects once the pores are filled with material of interest. To overcome these inconveniences, templates of uniform pore diameter were fabricated through a two-step anodization process [10]. Figure 1 (b) is a SEM micrograph of a fabricated alumina template. The structure of porous alumina can be described as self-ordered array of cells with cylindrical pores of diameter as low as 10 nm and depth exceeding 1000 μm [11,12]. The pore geometry can be controlled by the oxidization conditions. The templates were filled by pressure injection with molten Bi [13]. Figure 1(c) represents a SEM micrograph of an alumina template filled with Bi nanowires with a uniform pore diameter of 40 nm. A layer of excess Bi resulted from pressure injection process is present on one side of the sample. The thickness of these samples is typically tens of microns (50-70 μm) and consequently samples are very fragile and difficult to handle.

MEASUREMENT TECHNIQUE

The thermal diffusivity of alumina templates (empty or filled with Bi) was measured

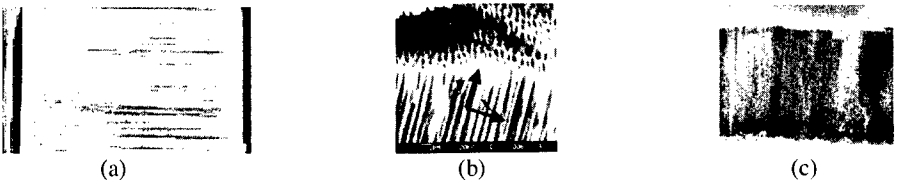

Figure 1. SEM micrographs: (a) Cross-section of a commercially available alumina template (0.02 μm Whatman, Anodisc). (b) Fabricated alumina template. y represent the direction along the pore axis and x represent the direction perpendicular to the pore axis.(c) Bi filled alumina template. The non-uniform top layer is excess Bi.

along the pore/nanowire axis (y-direction in Fig. 1(b)). Figure 2 shows a schematic of the experimental set up. In this technique, ac optical heating is applied at the front side of the sample and a fast thermoelectric effect is used to detect the temperature rise at the backside.

The ac heating is produced by the absorbed light coming from a tungsten lamp and modulated by a chopper. The area of the light spot is of few mm^2 in order to insure one-dimensional heat conduction across the sample thickness, which is in the order of tens of microns. In case of transparent samples (such as empty alumina templates) a thick copper layer (about 1μm thick) was deposited on the front side of the sample in order to absorb the incident light.

The amplitude and phase of the temperature signal are monitored at the backside by a fast responding thermocouple. The junction of the thermocouple consists of a point contact between a sharp metallic wire and the sample surface, which has to be electrically conductive [14,15]. Since the junction has zero thermal mass the thermocouple is expected to be very fast responding. Previous experiments carried out in our laboratory demonstrated that the thermocouple junction could respond to frequencies higher than 100 KHz [14,15]. A second wire is connected to the sample surface far from the heated spot in order to close the electrical circuit. The thermocouple voltage consists of the Seebeck voltage drop across the sharp wire (V_w in Fig. 2) and the in-plane Seebeck voltage drop on sample surface (V_s in Fig. 2). The second wire attached to the sample experiences no temperature difference between its ends and therefore has no contribution to the thermocouple voltage. The thermocouple voltage is measured by a lock-in amplifier at the modulation frequency. The data collection is automatically and controlled by a LabView program.

MODELING AND CALIBRATION

The modulated heating at the front side of the sample produces an AC temperature rise at the backside. Under the assumption of one-dimensional heat conduction and adiabatic boundary condition the complex temperature rise at the backside of the sample is given by:

$$T(L) = \frac{2Pe^{mL}}{Akm(1-e^{2mL})} \qquad (1)$$

where

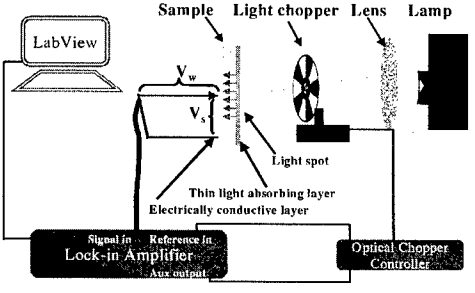

Figure 2. Experimental set-up.

$$m = \sqrt{i\frac{2\pi f}{\alpha}} \qquad (2)$$

and P is power, A is area, k is sample thermal conductivity, f is frequency, L is sample thickness and α is thermal diffusivity. The expression contains both the amplitude and phase of the temperature rise.

The thermal diffusivity can be determined by comparing the calculated phase and the normalized amplitude of the AC temperature rise with the experimental signal.

The technique was tested on glass slides (VWR International, Micro Cover Glasses) of two different thicknesses. The glass slides were covered by e-beam deposition with 1 μm of copper on one side to absorb the light and with a thin (500 nm) layer of gold on the other side for electrical conduction. Figure 3 (a and b) is an example of the normalized amplitude and phase for glass slides of two different thicknesses of 147 (±12) μm and 240 (±12) μm. The dots are experimental data and the continuous line is the fitting curve. The measured thermal diffusivity is $6.2\text{x}10^{-7}$ m^2s^{-1} for the 147 μm thickness sample and $5.6\text{x}10^{-7}m^2s^{-1}$ for the 240 μm sample. The difference in the measured thermal diffusivity could be explained by the relatively high uncertainty in the thickness measurement. The value of measured thermal diffusivity is relatively close to the one reported by a manufacturer (Corning) of similar type of glass: $6.9\text{x}10^{-7}$ m^2s^{-1}[16].

RESULTS

The thermal diffusivity characterization of commercially available (Whatman, Anodisc) empty alumina templates was performed first. Figure 4 (a and b) shows the experimental signals and the fitted phase and normalized amplitude for Whatman templates of two different pore diameter and porosities. The thermal diffusivity of the 0.02 μm pore diameter Whatman template (36% porosity) is found to be $5\text{x}10^{-7}$ m^2s^{-1}. The value is close to the thermal diffusivity of the 0.1 μm pore diameter template (50% porosity) $4.7\text{x}10^{-7}$ m^2s^{-1}. However, template roughness (estimated to be thousands of Å) may affect these results since the sharp wire may not be in good contact with the solid part of the template underneath. Currently, different methods are investigated in order to cross-check these results.

It should be mentioned that thermal conductivity of the 0.02 μm Whatman templates was measured through a different technique before [17]. In this technique a microfabricated heater/temperature sensor was used to measure the anisotropic thermal conductivity of the

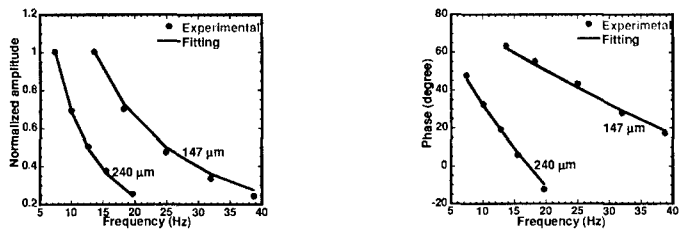

Figure 3. Normalized amplitude (a) and phase (b) of glass slides of two different thicknesses. The dots represent experimental data points and the continuous line is the fitting.

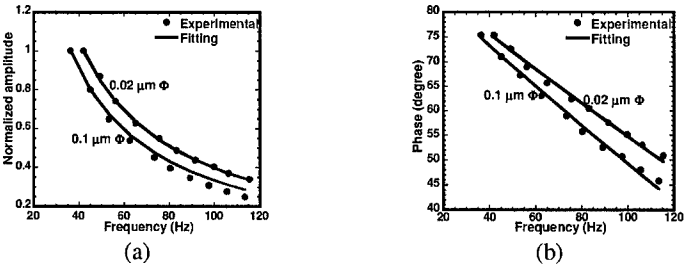

Figure 4. Normalized amplitude (a) and phase (b) of Whatman anodic alumina templates of 0.02 μm pore diameter (36 %) and 0.1 μm pore diameter (50% porosity).

template. The effective thermal conductivity measured along the pore axis was 1.47 W/mK. However this measurement required density/porosity and specific heat of amorphous porous alumina for data interpretation. Since these parameters were difficult to estimate a relatively high uncertainty remains associated with the above result. However, the low value of the measured thermal conductivity suggested that the alumina template is a good candidate for thermoelectric applications.

Finally the effective thermal diffusivity of Bi filled alumina template was measured. The excess Bi layer was used for electrical connection in thermocouple measurement. The incident light was directly absorbed at the other side of the sample. Figure 5 (a and b) shows the experimental signals and the fitted normalized amplitude and phase. Preliminary results suggest that thermal diffusivity of the filled sample is 1.3×10^{-6} $m^2 s^{-1}$. The calculated phase and normalized amplitude at low frequencies agrees well with the experimental data. However, at higher frequencies there is a difference between predictions and experiment. Although the reason for this is still under investigation a possible explanation could be the thermal mass of the Bi layer from the backside of the sample. It should be emphasized that this result is preliminary. The thermal diffusivity measurement was carried out on a single sample of relatively small size. More measurements on samples with different thicknesses and of larger area must be carried out in order to confirm the result. Furthermore, in order to extract the thermal diffusivity of Bi nanowires and compare it with thermal diffusivity of bulk Bi (8×10^{-6} $m^2 s^{-1}$), thermal diffusivity measurement of the fabricated template must be carried out.

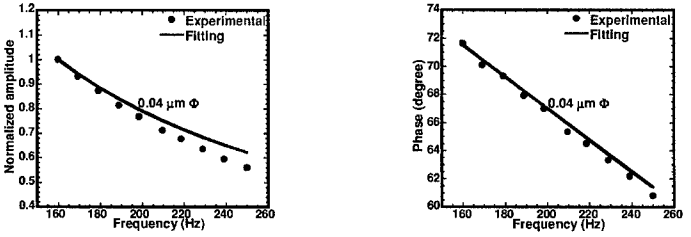

Figure 5. Normalized amplitude (a) and phase (b) of Bi filled alumina template.

CONCLUSION AND FUTURE WORK

A simple and fast technique was applied to characterize thermal properties of thin membranes. Thermal diffusivity measurements of Bi filled alumina template were carried out at room temperature. The results suggest that thermal diffusivity of the filled template is larger then thermal diffusivity of the empty alumina template. Currently, efforts are on way to characterize the 40 nm diameter template in order to extract the thermal diffusivity of Bi nanowires.

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