Fabrication of Bismuth Telluride Wire Thermoelectric Devices

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Abstract— **Bismuth telluride wires are interesting building blocks of thermoelectric devices. These are nanoscale heat to electric converters that have applications as uncooled detectors, generators and uncooled bolometers. Also, there is interest in bismuth telluride because it is an example of a topological insulator. The exploitation of the thermoelectric properties of devices based on wires of thermoelectric materials requires good electrical contacts between the wires and metal electrodes. The fabrication of the devices here, is based on contacting the wire ends to the device electrodes by depositing a platinum film using the focused ion beam method.**

***Keywords*— Thermoelectrics, bismuth, telluride, wire.**

I. INTRODUCTION

The science and technology of bismuth telluride (BiTe) wires has advanced to the point that many methods for fabrication and for characterization are available. There have been several reports of bismuth telluride wire fabrication by laser ablation [1]. Reports have also confirmed the synthesis of individual bismuth telluride wires by cyclic electrodeposition/stripping coupled with electrochemical step edge decoration [2] where the wire diameter is determined by processing variables. We believe that there is a simpler approach to define the wire diameter by separating the fabrication steps of wire synthesis and isolation; wires can be grown in arrays employing the template strategy where materials consisting of arrays of channels of the chosen diameter, such as porous anodic alumina or other nanochannel array, are injected with the melt of the chosen composition. One method of injecting the channels is electrodeposition into porous anodic alumina templates [3-6]. The high pressure injection (HPI) method is successful in preparing thick, dense, large-area Bi wire array composites [7]. The HPI method benefits from the substantial body of knowledge regarding the preparation of bulk Bi2Te3-Sb2Te3-Bi2Se3 alloys of both n-type and p-type of optimal composition for thermoelectric operation because these alloys are prepared traditionally by mixing in the molten state prior to crystallization. The thermoelectric properties of the wires can be measured employing microfabricated devices. Here we discuss the fabrication of a device where the wire is contacted at the two wire ends. Unlike the four point devices (two contacts for current and two for voltage), the two point device is sensitive to the contact resistance between wire and electrodes. Also, the two-point device is a way to prepare devices for applications and is more practical than four-point devices. We use this device to evaluate the wire thermoelectric properties and the contact resistance. The plan of this paper is as follows. In section II we discuss BiTe wire arrays and in Section III we discuss the methods employed for isolating individual BiTe wires in a two-point device and the contact resistance that is observed.

II. BISMUTH TELLURIDE WIRE ARRAYS

In this section we discuss the fabrication and characterization of BiTe wire arrays. We have employed a template method, the high pressure injection (HPI) method, where the melt of the alloy of interest is injected in the template using high pressure. For this work, we used a commercial alumina membrane solid for microfiltration under the trade name Anopore (Whatam Laboratory Division). Anopore consists of an alumina plate 25 mm in diameter and about 55 μm thick, which supports an array of 200-nm diameter, parallel, largely non interconnected, cylindrical channels running perpendicular to the plate surface.

In order to inject bismuth telluride in the pores we place high purity, 99.999%, Bi_2Te_3 pellets (Sigma-Aldrich) in contact with Anopore in a high pressure reactor. The reactor is heated to a temperature above the melting point of the material to be injected; in the experiments presented here, this temperature is 650°C. The pressure is then gradually raised to 1 kbar, forcing the molten material into the matrix channels. After a few minutes, when the injection is complete and the melt solidifies inside the channels, the reactor is cooled and the pressure is then released. The wire array sample is then extracted from the capsule and cleaned of the surrounding excess material by standard mechanical polishing techniques.

The crystal orientation of the wire sample was determined by X-ray diffraction (XRD) experiments with the reflecting planes normal to the wire axis. The observed peak positions are very close to the peak positions in bulk BiTe, and correspond to planes that are perpendicular to the c-axis. This indicates not only that the rhombohedral structure of bulk BiTe is preserved in these fine wires but that the wires in the array are

V. Sontea and I. Tiginyanu (eds.), *3rd International Conference on Nanotechnologies and Biomedical Engineering*,
IFMBE Proceedings 55,
DOI: 10.1007/978-981-287-736-9_23

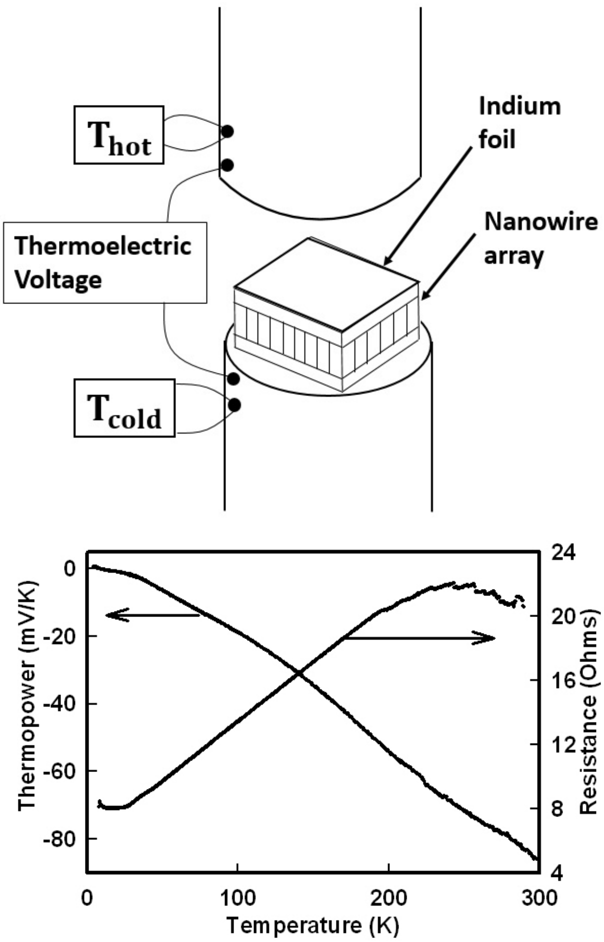

Fig. 1 Top: experimental equipment for wire array resistance and thermopower. Bottom: Temperature-dependent resistance R(T) and thermopower S(T) of a BiTe wire array. The number of wires contacted is unknown.

largely oriented with the c-axis perpendicular to the wire length. The resistance and thermopower of the arrays are measured by placing the sample, capped with indium foil, in a clamp designed to measure voltages and temperatures at either side of the clamp. Heaters establish a temperature difference between the clamp sides as required for thermopower measurements. This equipment is presented in the top of Fig.1. The wire's thermopower is negative (wires are type-n). The room temperature value is 90 μV/K .In comparison with the bulk that has $|S|$~200 μV/K, the thermopower is ~50% smaller in our case. Thermopower value is important for applications since the efficiency is ~ S^2. A recent paper by Hamdou *et al* [6] reports reaching a thermopower of -150 μV/K by using an annealing step after fabrication therefore we are not far off this target.

The individual wires in the present study are 200 nm; since the critical diameter for the semimetal to semiconductor transition SMSC transition in BiTe is roughly 2 nm [8], quantum confinement effects can be neglected and the Fermi surface of the carriers in the wire is roughly the same as in bulk BiTe of the same composition. However, the composition is not accurately known. Even though the material that we inject is pure Bi_2Te_3, the relative Bi/Te composition of the wires does not have to be stochiometric, which are 40 at% Bi and 60*at*% Te where "*at* " stands for atomic, due to Bi/Te differential surface tension. Composition control is a serious problem because the thermoelectric properties of BiTe are a strong function of the composition. (It only takes a 0.1% change in the Bi/Te ratio to change the material from type-p to type-n). The atomic composition of the arrays was studied with an S4500 Scanning electron microscope equipped with a Princeton Gamma-Tech EDX (Energy-dispersive X-ray) spectroscopy attachment. The wires are found to be stoichiometric within the precision of the measurement that is 1-3 %.

III. ISOLATING BITE WIRES

In this section we discuss the experimental methods employed for isolating a single wire of bismuth telluride.

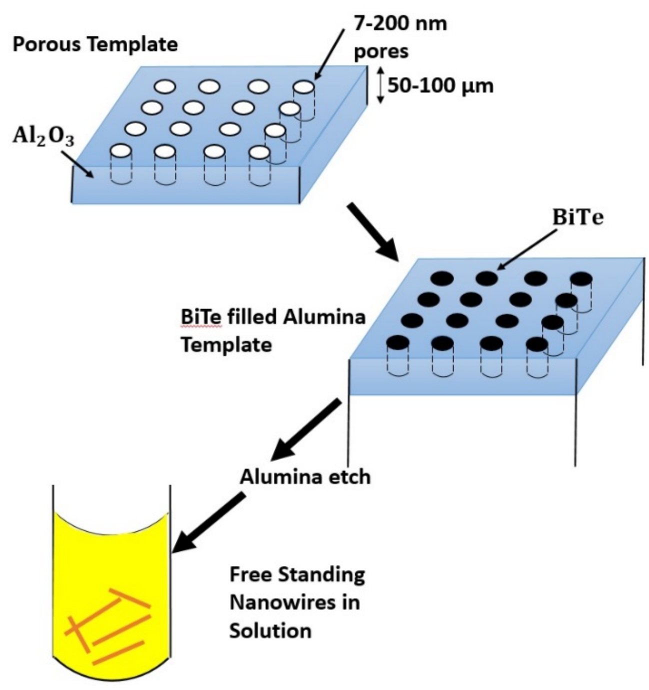

Fig. 2 Isolating individual BiTe wires via two steps; injection of bismuth telluride in aluminum template and etching the alumina using sodium hydroxide.

Removing the BiTe wires from the alumina template is difficult due to the chemical resilience of the alumina.

We employed a proven method [9] that consists of using a solution of 6N sodium hydroxide to dissolve the alumina while preserving the integrity of the BiTe wires.

The "solution" of wires is a good source of samples. To employ the solution, we deposited it with a pipette on the appropriate substrate: holey carbon for the SEM and TEM - experiments or patterned electrodes for the electrical measurements. The alcohol evaporates, leaving behind a sparse dispersion of wires that are loosely attached to the substrate. The individual BiTe wires were deposited on holey carbon for study with a 200 kV JEOL 2010F TEM with 0.25 nm resolution. This study will be discussed in a separate publication. Briefly, the selected area diffraction (SAD) pattern is consistent with the single crystal Bi_2Te_3 structure in PDF 15-863 and, therefore, consistent with the XRD study. Also consistent with the XRD study in Section II, we have found that the crystalline structure of the wire is oriented with the c-axis perpendicular to the wire length. SAD spots are dots in single crystalline material, as opposed to circular rings in polycrystalline materials or arc spots in textured structures. In fact we find that the wires are single crystalline along their whole length with few defects. A high resolution TEM image from the side wall of a Bi_2Te_3 wire is shown in Fig.3. The planes perpendicular to the <0001> direction are very clearly seen as horizontal lines (fringes) that are parallel to the side walls from this angle, therefore confirming that the c-axis is normal to the wire axis.

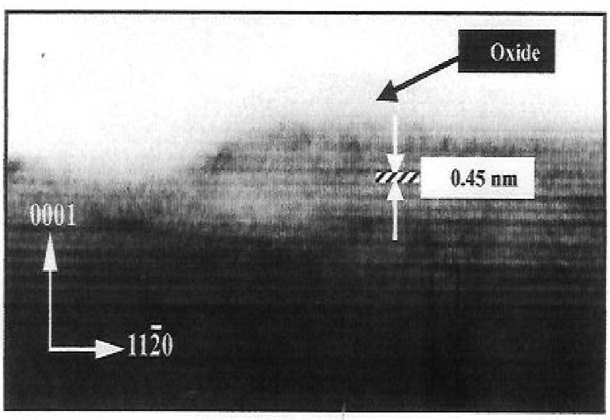

Fig. 3 High Resolution TEM image from the edge of a BiTe wire. The lattice fringes shown are (000L) planes where L=1,2,3,.. with an interplane distance of 0.5 nm for L=6. Fringes indicate that wires are single-crystal. The layer of oxide is clearly visible and is 1-2 nm thick. The image goes from clear to dark as we image the edge of wire.

The intensity of the image shows two periodicities, 0.5 and 1 nm, which correspond to the periodicity between planes perpendicular to the zone axis <0001>. The wires grown in the present study are single crystalline with few defects. The wire side walls are not smooth; they have sharp edges, but with ledges. This image shows an example of this morphology. A thin (1.5 nm) amorphous layer, presumably oxide, is observed along the side walls. The oxide layer is an important factor in achieving good electrical contacts to the wire. In the case of Bi wires [10], the presence of 7-nm thick oxide hampered the electrical measurements substantially.

In order to prepare a thermoelectric device we deposited a BiTe wire on patterned electrodes. The BiTe wire is electrically connected using a focused electron beam method. In this method, a conductive Pt composite joins wire and electrode. An example of the device that was assembled is shown in Fig.4. The resistance that is measured between the planar electrodes has contributions from the wire, from the Pt deposits and from the contacts. The current I as a function of applied voltage V was measured. The curves I=I(V) (I-V) were found to be non-linear, with a degree of nonlinearity that increases for decreasing temperature. This temperature-dependent non-linear response is believed to be due to the contacts between the wires and the gold electrodes. A thin insulating layer would provide a tunnel barrier for the electrons passing through it. Similar phenomena is observed by Cronin in Bi [10].

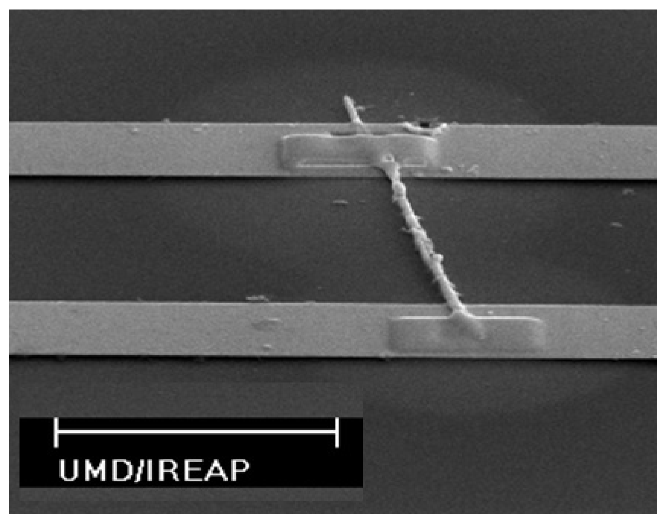

Fig. 4 Scanning electron microscope image of the two-point device. The gray bands are Au planar electrodes. The wire bridges two planar electrodes. The two light gray areas at the joint between planar electrodes and wire are Pt deposits. The wire is 200 nm in diameter, electrodes are 1 μm wide, and the distance between electrodes is 4 μm.

The room temperature contact resistance is 70 KOhms. We have observed that the characteristics of the I(V) curve at all temperatures depend upon the prior exposure of the wire to air and temperature.

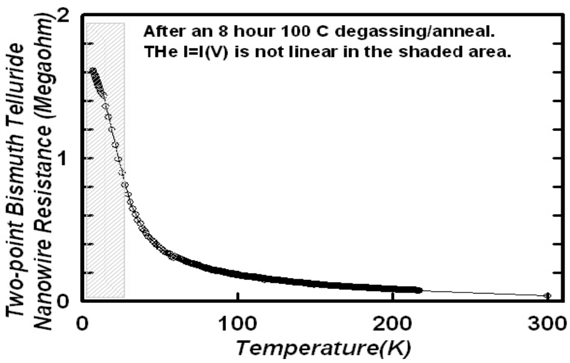

Fig. 5 R (T) of wires after an anneal/degassing.

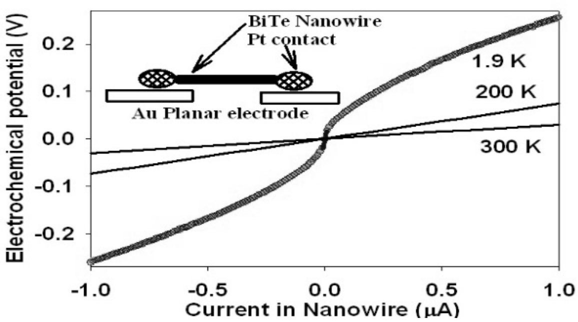

Fig. 6 I (V) of wires at various temperatures.

IV. CONCLUSIONS

We have fabricated a thermoelectric device based on 200-nm BiTe wires. The wires have been characterized as a part of the wire array. As shown in Fig.5 and 6, the wire electrical properties appear to be sensitive to air (oxygen). To test this property, we developed a procedure of degassing at modest temperatures (100 ºC) conditions the wire two-point device. At that point and at room temperature, the wire current is not limited by the rate of tunneling through the Pt contacts at either end of the wire. We believe that further gains can be achieved by conditioning at a higher temperature and by degassing in a hydrogen atmosphere.

ACKNOWLEDGMENTS

We thank M. Ervin, ARL and J. Melngailis and J. Barry of the University of Maryland. This material is based upon work supported by the National Science Foundation through Partnership for Research and Education in Materials DMR-1205608 and Science and Technology Center DMR-1231319. We also acknowledge The Boeing Co, the Swiss National Science Foundation and the Science Technology Center in Ukraine # 5986. We also acknowledge Jeffrey H. Hunt and John H. Belk of the Boeing Company for their contribution to developing this technology.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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