SYNTHESIS OF SINGLE CRYSTAL BISMUTH-TELLURIDE AND LEAD-TELLURIDE NANOWIRES FOR NEW THERMOELECTRIC MATERIALS

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ABSTRACT

Dimensionality can play an important role in determining the properties of materials. In the case of thermoelectric materials, it has been proposed that one-dimensional quantum wires, or nanowires, and two-dimensional superlattices could exhibit substantially higher efficiencies compared to the corresponding bulk, three-dimensional solids. To explore such predictions we have initiated a program directed towards the controlled growth of nanowires, and herein, we report the synthesis of single crystal Bi_2Te_3 and PbTe nanowires by a pulsed laser ablation method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that Bi_2Te_3 wires 80 nm to 200 nm in diameter and lengths exceeding 10 microns, and PbTe wires 25 nm to 60 nm in diameter and lengths to 2 microns can be readily produced by the laser ablation method. High-resolution TEM and electron diffraction show that Bi_2Te_3 nanowires are single crystals with wire axes along the <110> crystal direction. TEM and electron diffraction measurements also show that the PbTe nanowires are single crystals with a <100> growth axis. The transport properties of these new nanowire materials will be discussed.

INTRODUCTION

There has been considerable interest in the past few years in finding new thermoelectric materials for use in solid state refrigerators with no moving parts [1]. The efficiency of a thermoelectric solid is found to depend on material properties through the dimensionless figure of merit ZT [2]. It is defined by $ZT = \sigma S^2 T/\kappa$, where σ is the electrical conductivity, S the Seebeck coefficient, or thermoelectric power, T the temperature, and κ the thermal conductivity. For a material to be a good thermoelectric cooler it must have a high ZT at room temperature and below. In general, it is difficult to improve ZT, because increases in the electrical conductivity for simple materials also lead to a simultaneous decrease in the thermoelectric power and a comparable increase in the electronic contribution to the thermal conductivity. Currently, the materials with the highest ZT are alloys based on Bi_2Te_3 with ZT near 1 at 300 K [2]. Bi_2Te_3 is the most important thermoelectric material that works below T = 300 K. However, the efficiency is rather low compared to freon-based compressors, and it can not be used to cool below 160 K [1, 3]. Therefore, there is a pressing need for new materials with higher efficiencies.

Dimensionality can play an important role in determining the properties of materials. The reduction of dimensionality from 3D to 1D results in a dramatic increase in the electronic density of states (DOS) at near energy band edges. In thermoelectrics it is known [3] that the power factor, σS^2, increases with DOS. Therefore, the increased DOS of 1D structures is predicted to produce an enhanced power factor, and consequently, an enhanced ZT. In addition, there will be increased phonon scattering from the surfaces of 1D wires. This will lead to a reduction in the lattice thermal conductivity and hence an increase in ZT. There have been several theoretical calculations [4, 5] reported that support these ideas. To explore such predictions experimentally we have initiated a program directed towards the controlled growth of nanowires, and herein, we report the synthesis of single crystal Bi_2Te_3 and PbTe (another important thermoelectric material) nanowires by a laser ablation method [6-8].

Mat. Res. Soc. Symp. Proc. Vol. 581

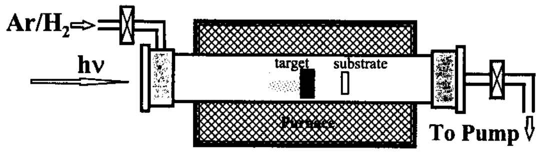

Figure 1. Schematic of the nanowire growth apparatus.

EXPERIMENTAL METHODS

Synthesis of Nanowires

Pulsed laser ablation (Spectra Physics GCR-16s, 355 nm or 532 nm) of targets composed of Bi_2Te_3 or PbTe was used to generate nanoclusters for 1D growth at thermodynamic non-equilibrium conditions. The growth apparatus is shown schematically in figure 1. The pressure in the growth chamber was kept at 100 – 250 torr. A mixture of Ar and H_2 (10% H_2) was used as a buffer gas with a flow rate of about 100 sccm. The growth temperature is 530 °C for Bi_2Te_3, and 815 °C for PbTe. The products were collected on a substrate located behind the target.

Structural Characterization of Nanowires

The morphology and structure of the products were examined by field-emission scanning electron microscopy (SEM) (LEO 982), high-resolution transmission electron microscopy (TEM) and electron diffraction (Philips EM420). Energy dispersive X-ray (EDX) spectra were recorded with the TEM to evaluate the elemental compositions.

Electrical Conductivity Measurement of Single Bi_2Te_3 Nanowires

After registering the position of single Bi_2Te_3 nanowires on oxidized Si substrates under SEM (JEOL JSM6400), electron beam resist was spun over the substrates and electron-beam lithography was used to define electrical leads to individual nanowires. After metalization of the leads I-V curves were obtained using Keithley 6517 electrometer and Keithley 220 programmable current source.

RESULTS

Bi_2Te_3 nanowires can be reproducibly prepared via vapor phase growth using our laser ablation method. Figure 2 shows SEM images of Bi_2Te_3 nanowires at different magnifications. They are faceted nanowires with diameters of 80 nm to 200 nm and lengths exceeding 10 μm. TEM and electron diffraction studies (figure 3) show that the nanowires are single crystals. The diffraction pattern can be indexed to the hexagonal lattice of Bi_2Te_3 (a = 4.385 Å, c = 30.48 Å) with the electron beam direction along [001] zone axis. A schematic illustration of Bi_2Te_3 structure viewed along the c axis superimposed on the TEM image of Bi_2Te_3 nanowire is shown in figure 3. These data show that the nanowires grow along the <110> crystal direction. The single crystal nature and growth direction are further confirmed by high-resolution TEM measurements (figure 4). The lattice fringes in figure 4 are (101) crystal planes with an inter-

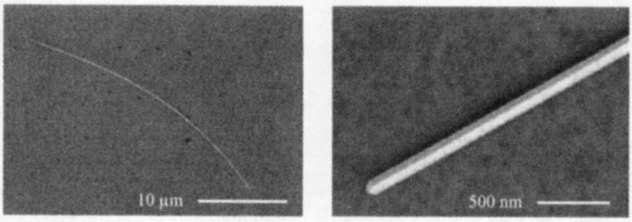

Figure 2. SEM images of Bi_2Te_3 nanowires.

plane distance of 3.80 Å. The angle between the fringes and the nanowire edge is 60°, which is expected from the <110> growth direction. EDX measurements show no other heavy elements except Bi and Te. Average atomic ratio of Te to Bi from 6 samples is 1.46. It gives a formula of $Bi_2Te_{2.92}$. The deviation from Bi_2Te_3 is within our experimental error.

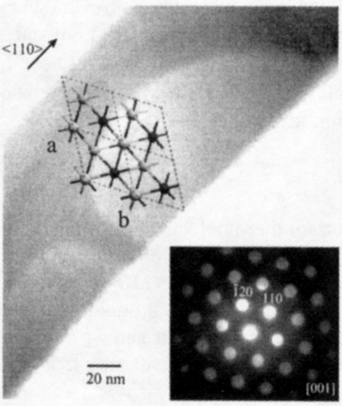

Figure 3. TEM image of a portion of Bi_2Te_3 nanowire with a schematic view of the Bi_2Te_3 structure in the ab plane superimposed on it. (inset) Electron diffraction pattern recorded along [001] zone axis.

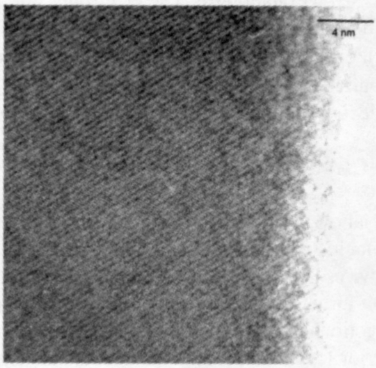

Figure 4. High-resolution TEM micrograph of the Bi_2Te_3 nanowire. The lattice fringes shown are (101) planes with an inter-plane distance of 3.80 Å. The angle between the fringes and the wire edge is 60°.

Similar results are obtained for PbTe nanowires. PbTe nanowires are 25 nm to 60 nm in diameter with lengths to 2 μm and can be readily produced. Figure 5 shows the TEM micrograph of one PbTe nanowire and its electron diffraction pattern. The diffraction pattern can be indexed to the face-center cubic structure of PbTe (a = 6.443 Å) with the electron beam along the [001] zone axis. These data show that the PbTe nanowires are single crystals and grow along the <100> crystal direction. EDX measurements from 5 samples give an average atomic ratio of Pb to Te as 1:1.01.

To evaluate the intrinsic thermoelectric figure of merit, the properties of individual nanowires must be measured. The electrical conductivity, σ, and thermoelectric power, S, can be

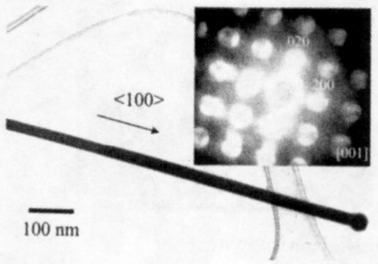

Figure 5. TEM image of a PbTe nanowire. (inset) Electron diffraction pattern recorded along [001] zone axis.

determined from transport measurements using micro/nanofabricated electrodes. Below are the preliminary results of electrical conductivity measurements of individual single crystal Bi_2Te_3 nanowires. Electrodes defined by electron-beam lithography can be routinely fabricated on the desired individual nanowires. Figure 6 shows a SEM image of lithographically defined Au leads on one Bi_2Te_3 nanowire. The electrodes are usually separated by 2 μm to 10 μm. An I-V curve obtained at room temperature on a portion of Bi_2Te_3 nanowire with diameter of 120 nm and length of 13 μm is shown in figure 7. The resistivity determined for this wire, 1400 μΩ·cm, is comparable to the literature value for Bi_2Te_3 single crystals, 1700 μΩ·cm [3]. The dependence of the electrical conductivity on temperature is currently being investigated.

CONCLUSIONS

Nanowires of Bi_2Te_3 and PbTe, two of the most important thermoelectric materials for thermoelectric refrigeration, have been successfully synthesized by a laser ablation method. Both nanowires have high aspect ratios and are single crystals. They grow along <110> direction and <100> direction, respectively. E-beam lithography has been used to make reproducible connections to these nanostructures, and preliminary transport measurements show promising behavior for these 1D structures. It is also expected that increased phonon scattering from the

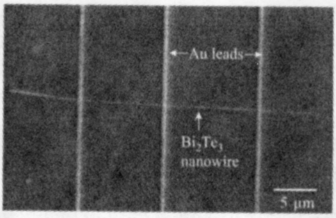

Figure 6. SEM image of lithographically defined electrodes on top of a single Bi_2Te_3 nanowire.

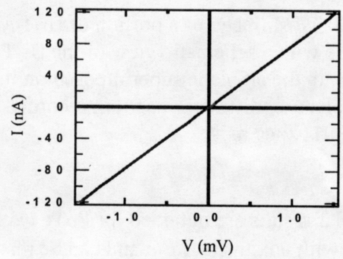

Figure 7. I-V curve from a portion of single Bi_2Te_3 nanowire with diameter of 120 nm and length of 13 μm at room temperature. The resistivity of this nanowire is 1400 μΩ·cm at room temperature.

surfaces of the nanowires will significantly lower the thermal conductivity, and hence enhance the thermoelectric figure of merit. An approach for measuring the thermal conductivity of individual nanowires is being developed in our laboratory. Studies of the transport properties of these individual nanowires will enable us to better understand the fundamental physics of 1D structures.

ACKNOWLEDGMENTS

We thank Y. Lu for help with TEM. C.M.L. acknowledges support of this work by the Office of Naval Research.

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