In-situ TEM Study of Bismuth Nanostructures

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ABSTRACT

Nanostructured thermoelectric materials have attracted lots of interest in recent years, due to their enhanced performance determined by their thermoelectric dimensionless figure of merit. However, because of equipment limitations, not much work has been done on combining simultaneous transport measurements and structural characterization on individual nanostructured thermoelectric materials. With an integrated TEM-STM system, we studied the structural behavior and electrical properties of bismuth (Bi) nanobelts and nanoparticles. Results showed that clean Bi nanostructures free of oxides can be produced by in-situ high temperature electro-migration and Joule annealing processes occurring within the electron microscope. Preliminary electrical measurements indicate a conductivity of two orders of magnitude lower for Bi nanoparticles than that for bulk Bi. Such in-situ studies are highly advantageous for studying the semimetal-semiconductor transition and how this transition could enhance thermoelectric properties.

INTRODUCTION

The anisotropic electronic structure of Bi provides some directions along the constant energy surfaces for the three electron pockets at the L point of the Brillouin zone which have very low effective mass components giving rise to high mobility carriers. At the same time, the constant energy surfaces have other directions with heavy masses giving rise to a high density of states effective mass. For both of these reasons, very good thermoelectric properties should be obtained for carrier transport along the low mass direction. However, as the size of a Bi nanowire or nanoparticle become smaller, the lowest quantized level in the conduction band moves up in energy and the highest quantized level in the valence band moves down, so that eventually these levels cross and a semimetal to semiconductor transition occurs. This transition occurs for larger diameter nanostructures as the temperature is decreased or as Sb is added in the structure up to about 10%. In the semiconducting state, transport by electrons and not by holes can be achieved by n-type doping, thereby allowing us to capture the benefits of the anisotropic constant energy surfaces of the L point carriers in Bi. The heavy atomic mass of Bi also results in a low thermal conductivity which is also desirable for good thermoelectric performance.

Studies at the single nanowire and single particle level are necessary to probe the anisotropic aspects of these anisotropic constant energy surfaces. Experiments inside a
transmission electron microscope, such as are described in this paper, allow us to produce clean Bi nanostructures free of oxides, and to study both their structural and electronic properties at the same time. This is highly advantageous for studying the semimetal-semiconductor transition and how this transition could enhance the thermoelectric properties of this materials system.

Electrical transport measurements of individual nanowires and nanoparticles have always been challenging, especially for very fine Bi nanostructures (diameters < 100nm) due to both their tendency to oxidize easily and their poor mechanical properties [1]. Here we present a direct approach to make single nanowire or nanoparticle measurements with an in-situ TEM-STM system based on a JOEL 2010F HRTEM instrument which is integrated with a Nanofactory STM holder. As shown in Figure 1, the suspended nanowires or nanoparticles on the sample holder (which also serve as one electrode) can be approached and contacted by the STM probe. The movement of the STM tip is controlled by piezoelectric materials, and the STM tip can be observed under the TEM. With this setup, we are able to make electrical measurements on nanostructures with different sizes and morphologies, while imaging the nanostructures simultaneously.

Figure 1. Schematic diagram of the in-situ TEM-STM system used to make simultaneous electrical and structural measurements [6].

EXPERIMENT

Materials preparation

One-dimensional Bi nanowires are usually prepared using rigid inorganic or polymer templates. Here we prepared Bi nanobelts and nanoparticles by a polyol process, which provides good shape control of the synthesized nanostructures. Nanobelts with an average width of ~60nm and nanocubes with an average edge length of 60-80nm were synthesized by this basic process [2]. Bi nanoparticles with an edge length as small as 3.8nm can also be grown within the HRTEM chamber as described below.

Bi nanobelts

As stated above, the two biggest challenges for Bi nanobelt measurements are removing the thick oxide layer surrounding the nanobelt without destroying the Bi core, and making good low contact resistance electrical contacts between the nanobelt and the electrode. Within the TEM high vacuum chamber, we successfully removed the oxide shell surrounding the Bi nanobelt by applying an electrical bias. Successive steps in the reaction process are shown in
Figure 2 and Figure 3. Before applying a bias, a 19.6 nm wide, 50 nm long Bi nanobelt inside a 7.2 nm oxide layer is placed in contact with a gold STM probe and the other electrode, respectively. The measured lattice spacing and selected area diffraction pattern indicate the crystalline structure of the Bi core region to be along a <012> direction. After applying a ~3V bias for Joule heating for ~3min, the oxide shell disappears gradually, while the Bi core starts to expand. No crystalline structure of the nanobelt was observed during this process. Shortly after this transformation starts, the shell layer surrounding the entire wire disappears, and the measured current under constant applied bias is increased, indicating the disappearance of oxide layer. Upon fast quenching to room temperature (achieved by cutting off the bias current), a single crystalline Bi structure along the <012> direction was observed for the nanobelt (see Figure 3). The bias voltage should be controlled carefully, because once the reaction finishes, the current remains high, and the entire Bi nanobelt could melt.

**Figure 2. Before Joule heating annealing:** The Bi nanobelt (surrounded by the Bi oxide shell) in contact with the gold electrode shown at low resolution (left) and higher resolution (right). Inset is a select area diffraction pattern of the Bi core.

**Figure 3. After Joule heating annealing:** The Bi oxide shell disappears, and finally the nanobelt becomes an almost pure crystalline Bi structure oriented along a <012> direction (right).

**Bi nanoparticles**

Bi nanoparticles are also a good candidate for studying quantum size effects, because they provide more quantum confined structures, and because a wide distribution of particle sizes and some choices in crystalline orientations can be readily achieved. However, conventionally
grown Bi nanoparticles are always embedded in a surfactant solution, in order to prevent aggregation and oxidation. Thus Bi quantum dot electrical measurements become very challenging, and no electrical measurements for individual Bi quantum dots have so far been reported to our knowledge.

With our setup, we were able, starting from big Bi particles, to grow clean Bi nanoparticles, with different sizes and crystalline orientations, by applying a dc bias using the setup shown in Figure 4. As we increase the bias, the current density at the tip/Bi contact is increased. Then, by slowly moving the STM tip away from the big particle of Bi, a clean Bi nanoparticle is formed (Figure 4), with the nanoparticle in good contact with both the STM tip and the Bi big particle. Figure 4 shows a 10 nm by 3.8 nm Bi nanoparticle along the <101> direction (left) and a 10 nm by 8 nm Bi nanoparticle along the <012> direction (right) grown within the TEM chamber in another experiment done in the same set-up.

**Figure 4.** A 10nm×3.8nm Bi nanoparticle oriented along the <101> direction (left) and a 10nm×8nm Bi nanoparticle oriented along the <012> direction (right) were grown from bulk Bi upon applying a bias voltage between the STM tip and the big Bi particle.

**Preliminary electrical characterizations**

Figure 5 shows the measured I-V curve for a 20.4 nm (wide) by 7.7 nm (long) nanoparticle between two electrodes. From the data in Figure 5, a conductance of 7.8×10⁻⁵ S is obtained which correspond to a conductivity of 2×10³ S/m if we assume that the particle has a circular cross section. For all the nanoparticles measured, the conductivities range from 2×10³ to 8×10³ S/m, which is about two orders of magnitude lower than that of the bulk Bi conductivity of ~ 8×10⁵ S/m. The drop in conductivity in nano Bi may be due to a reduced carrier concentration arising from quantum confinement effects.

**Figure 5.** Measured I-V characteristics for a 20.4 nm (long) by 7.7 nm (wide) Bi nanoparticle.
DISCUSSION

Thermodynamics for Bi oxide reduction

Figure 2 and Figure 3 show that when a current is passed through the nanowire, a phase transition occurs where the oxide layer surrounding the Bi core is changed into Bi following Eq.1. The reaction takes place first close to the connection between the wire and tip of the STM. This is to be expected since the contact resistance between the tip and the wire will give rise to a local increase of temperature that will eventually favor the following reaction:

\[
\text{Bi}_2\text{O}_3(s/l) \rightleftharpoons \frac{3}{2} \text{O}_2(g) + 2\text{Bi}(l)
\]

in which, \(s\), \(l\) and \(g\) denote solid, liquid and gas phases. As seen in Figure 3, the Bi nanowire initially melts when the temperature reaches 545K. Even if \(\text{Bi}_2\text{O}_3\) is stable with liquid Bi and oxygen under normal conditions, temperature increase because of the current and the reduced oxygen pressure in the vacuum chamber of the TEM will eventually favor the decomposition of the oxide. Omitting energy barrier considerations, the reaction to the right will be spontaneous when the Gibbs free energy for \(\text{Bi}_2\text{O}_3\) formation (\(\Delta G\)) becomes positive. Following [3], the free energy of formation of \(\text{Bi}_2\text{O}_3\) is:

\[
\Delta G^\circ(kJ/mol) = -583.4 + .2938T(572K \leq T \leq 988K)
\]

\[
\Delta G^\circ(kJ/mol) = -543.8 + .2538T(988K \leq T \leq 1098K).
\]

Because of the reduced oxygen pressure in the vacuum chamber of the TEM, a pressure term correction must be added to the free energy and the free energy of formation becomes [4]

\[
\Delta G = \Delta G^\circ - RT \ln \left( \frac{P_{\text{O}_2}^{3/2} a_{\text{Bi}}^2}{a_{\text{Bi}_2\text{O}_3}} \right)
\]

where \(R\) is the ideal gas constant, \(T\) is the temperature, \(P_{\text{O}_2}\) is approximated as the pressure in the TEM chamber and \(a_i\)'s are the activity coefficient of the Bi and the \(\text{Bi}_2\text{O}_3\) that we take as one under the assumption that they are perfect liquid and a perfect solid [5]. Figure 6 shows the result of this calculations and it demonstrates that for temperature above 1003K, we should expect a decomposition of the \(\text{Bi}_2\text{O}_3\) external layer into Bi. It also becomes evident that the high temperature needed to convert the oxide layer will be more than sufficient to locally melt the Bi core. This melting weakens the nanowire and explains why failure to remove the voltage bias after the complete \(\text{Bi}_2\text{O}_3\) to Bi transition could lead to a decomposition of the wire.
Free energy of formation of Bi₂O₃. Free energy of formation of Bi₂O₃ as a function of temperature under an oxygen pressure of 10⁻⁵Pa. At ~1003K, the free energy of formation becomes positive which means that the decomposition of Bi₂O₃ will be favored and spontaneous, once the energy barriers are removed.

**Bi nanoparticle in-situ growth**

As we know, Bi is a very low melting point material with a bulk melting point of 271°C, and the electro-migration of Bi could happen at a current density as low as 300A/cm². As we increase the applied bias, the temperature at the electrical contact increases dramatically as the current increases sharply, due to the Joule heating caused by the contact resistance. Thus the Bi atoms become mobile. Meanwhile, the current density reaches a high value of 2.5×10⁶A/cm² so that the electro-migration of Bi becomes very strong near the electrical contact. For this reason the nanoparticle growth is due to electro-migration of Bi under high current density.

By controlling the current density and the speed of the STM tip movement, Bi nanoparticles with different sizes and orientations are grown. This gives us the feasibility of growing clean Bi nanoparticles with a wide size distribution, and studying their electrical properties at the single nanoparticle level, while measuring its structure in the TEM.

**CONCLUSIONS**

We have here demonstrated a direct approach to reduce the oxide layer surrounding Bi nanobelts by high temperature annealing using Joule heating of the nanobelt in a TEM-STM system. This non-destructive method is good for measuring very fine Bi nanowires, and may also be applied to single nanowire measurements on a variety of materials in other high vacuum systems. We also demonstrate for the first time TEM in-situ growth of Bi nanoparticles by Joule heating and electro-migration. The clean various-sized particles are ideal for study of quantum size effects. Our first electrical measurements showed that the electrical conductivity of Bi nanoparticles is two orders of magnitude lower than that of bulk Bi, likely due to quantum size effects that decrease the carrier concentration. Further experiments are needed for investigating the size and crystalline orientation dependences of the electrical conductivity. This work forms a baseline for future thermoelectric measurements on Bi nanostructures.
ACKNOWLEDGMENTS

Support for this work was provided by NSF-NIRT Grant number CBET-0506830. We are grateful for helpful discussions with Dr. Gene Dresselhaus and Prof. Carl V. Thompson.

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