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Description	

True Atomic Level Imaging of Shaped Nanoparticles Composed of Bismuth, Antimony and Tellurium using Scanning Transmission Electron Microscopy.

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ABSTRACT

Nanotechnology is an area of research that is highly intriguing because of the novel properties often observed for materials whose sizes are reduced to the nanoscale. However, one of the biggest challenges is understanding the underlying principles that dictate the particles resulting properties. The atomic level structure for nanoparticles is suspected to vary from that for the corresponding bulk materials, however, direct observation of this phenomenon has proven difficult. Until recently only indirect information on the atomic level structure of such materials could be obtained with techniques such as XRD, HR-TEM, XPS, etc… However, recent advances in Transmission Electron Microscopy techniques now allow true atomic scale resolution, leading to definitive confirmation of the atomic structure. Namely, Scanning Transmission Electron Microscopy coupled with a High-angle Annular Dark Field detector (STEM-HAADF) has been demonstrated to be capable of achieving a nominal resolution of 0.8 nm (the JEOL JEM-ARM200F instrument). The ability is highly exciting because it will lead to an enhanced understanding of the relationship between atomic structure of nanoparticles and the resulting novel properties. In our own study, we focus on the analysis of the atomic level structure for nanoparticles composed of bismuth, antimony and tellurium for thermoelectric materials. This area has recently received much interest because of the realization that nanotechnology can be employed to greatly enhance the efficiency (dimensionless figure of merit ZT) of this class of materials. One of the most intriguing parameters leading to the enhanced TE activity is the relationship between composition and structure that exists within individual nanoparticles. We report our results on a study of the atomic level structure for both nanowires and nanodiscs composed of bismuth, antimony and tellurium. It was found that the nanoparticles have a complex structure that cannot be elucidated by conventional techniques such as XRD or HR-TEM. In addition, by employing Energy Dispersive Spectroscopy (EDS), a greater understanding of the composition-structure dependence was gained. The results are primarily discussed in terms of the atomic level resolution images obtained with the STEM-HAADF technique.

INTRODUCTION

Transmission Electron Microscopy (TEM) is an incredibly powerful technique in the field of nanotechnology. By utilizing a focused beam of electrons to form a visual image, much higher magnifications have been achieved than is possible with optical microscopes. Despite the importance of the TEM technique in providing key definitive information in addressing nanoscale size and shape properties for materials, there has always been some disappointment because the resolution reached has never approached that theoretically predicted. This is primarily because of challenges in focusing the electron beam using magnetic lenses, achieving high vacuum levels, and maintaining stable high voltage sources for the instrument. Over time however, the technology has advanced with High Resolution TEM becoming commonplace.

Recently there has been another breakthrough in TEM technology. The use of Scanning TEM (where the electron beam is rastered over the sample) in conjunction with a High Angle Annular Dark Field Detector (HAADF) has resulted in images with unprecedented resolution (0.8 Å nominal) [1]. The HAADF detector also offers enhanced Z-contrast for the sample, with different types of atoms being able to be differentiated in the resulting image [2]. The technique has enabled true atomic level imaging and opens the door to correlating the atomic structure of nanoparticles with their exhibited new and enhanced properties. Thermoelectrics (TE) are one such class of material that has been demonstrated to have enhanced properties on the nanoscale [3]. The creation of TE materials with a nanoscale structure increases the phonon scattering along grain boundaries, ultimately suppressing the thermal conductivity, which increases the thermoelectric efficiency (ZT value) of the material [4]. In our own previous research we have successfully synthesized nanoparticles containing bismuth, antimony and tellurium with both nanowire and nanodisc shapes. However, the resulting composition, structure, and shape properties were complex, making it a challenge to correlate the resulting TE properties [5]. By analyzing these promising materials using the STEM-HAADF technique, we seek to gain insight into the relationship between atomic structure and the resulting material properties.

EXPERIMENT

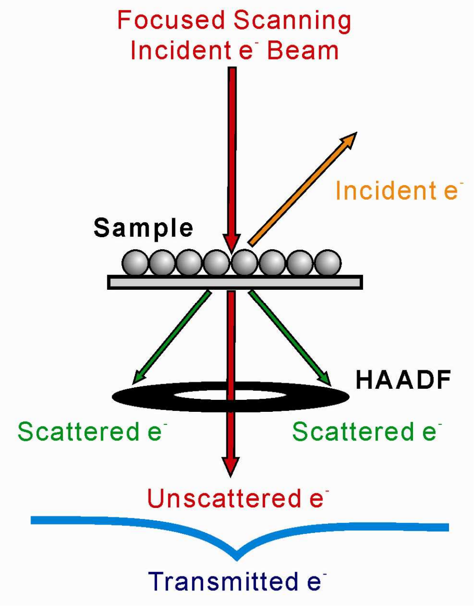
Chemicals: bismuth trichloride, antimony trichloride, tellurium tetrachloride, oleic acid, oleylamine, 1,2-hexadecanediol, 1-decanethiol and di-octylether as well as other common solvents were obtained from Aldrich.

S*ynthetic Technique:* $1.67\text{x}10^{-4}$ moles each of bismuth, antimony and tellurium precursors was mixed with 25 ml di-octylether, then $1.5\text{x}10^{-3}$ moles of 1,2-hexadecanediol was added along with the capping species, the identity of which was used to manipulate the morphology of the resulting nanostructures. For the synthesis of nanowires, 0.16 ml of oleic acid and 0.17 ml of oleylamine were used. For the synthesis of nanodiscs, 1.5 ml of 1-decanethiol was used as capping agent. The mixture was purged with argon under vigorous stirring. At this point the mixture temperature was raised to 105 ^{o}C for 10 minutes to remove water, which also caused the reactants to completely dissolve in the solvent (a light grey color in the solution). After this, the temperature was increased to 200 ^{o}C and was held for 1 hour. The formation of particles within this time was evidenced by the solution color change from light grey to dark grey or black depending on the capping species used. After reaction, the nanoparticle solution was cooled to room temperature and the particles were purified by precipitation in ethanol. The resulting nanomaterials were then analyzed.

Instrumentation and Measurements: The nanoparticles were studied using STEM-HAADF on a JEOL JEM-ARM200F instrument operated at 200 kV with nominal resolution of 0.8 Å. TEM images were obtained on an Hitachi H-9000NAR instrument. The samples for TEM and STEM-HAADF were prepared by dropping the suspended particles onto a carbon coated copper grid and drying in air overnight.

DISCUSSION

The results are discussed primarily in terms of studying the atomic structure for the two different shapes of nanoparticles composed of bismuth, antimony and tellurium. The STEM instrument provides definitive characterization of the atomic level structure. The synthesis and general characterization for these materials has been conducted previously, so is not repeated here. In this study, these unique nanoparticles are analysed using the STEM-HAADF technique to gain an understanding of the atomic level structure. The STEM-HAADF technique is fundamentally different from traditional TEM in that a focused electron beam is rastered across the sample, the electrons maybe backscattered, scattered, or can be unscattered, transmitting through the sample. The electrons that are inelastically scattered are detected by the HAADF detector and are used to form the image. Scheme 1 shows the basic STEM-HAADF technique.



Scheme1: A basic scheme of the STEM-HAADF instrumental technique. The image is formed from the inelastically scattered electrons incident on the HAADF detector.

Figure 1 shows two representative TEM images collected for the nanowires and nanodiscs. Figure 1A is a TEM image for nanowires synthesized using OAC/OAM capping species. The synthesis method and resulting characterization including particle size, shape and composition have been reported previously, so is not repeated in detail here [5]. In short, the nanowires have a micron length (~3-5 microns) scale and the diameter ranges from about 20 to 50 nm. The aspect ratio is quite high (~100x) as well as the shape monodispersity with only nanowires observed. The nanowires have light and dark striations that arise as a result of physical stress in the wire that develops as the particles are deposited onto the TEM grid. Figure 1B shows the TEM image of nanodiscs synthesized using decanethiol capping species. In the image several discs are standing on edge with some lying on face. The particles have a disc morphology with a diameter of about 100 nm and thickness of about 25 nm. These particles are also highly monodisperse in shape with only discs observed.

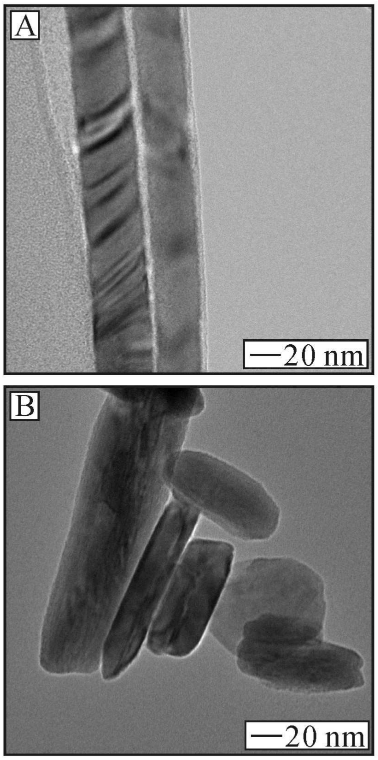


Figure 1: TEM images of nanowires synthesized with OAC/OAM (A) and nanodiscs synthesized with DT (B).

Figure 2 shows a STEM-HAADF image taken for the nanowires. The image was taken in roughly the center of a nanowire deposited longitudinally on the carbon coated grid. The white dots in the image represent atoms in the sample (a dark field image). The dark line that is observed running down the center of the particle arises from a twin plane, where two crystalline faces in the particle meet. The particle itself is highly monocrystalline with no evidence of defects. The inset to the figure and accompanying scheme represent the unit cell for the material which was determined based on measuring the interatomic distance for different crystalline planes in the sample. The material was found to have a hexagonal structure with 100 plane interlayer spacing of 3.70 Å and a c-axis value of 5.93 Å, which corresponds to monoelemental tellurium [6]. The corresponding scheme in Fig. 2 shows the corresponding atomic structure of hexagonal phase tellurium, and indicates the c-axis value. Previous study revealed these particles to contain elemental tellurium and Bi_2Te_3 present. The result obtained here is consistent with the previous characterization; the Bi_2Te_3 phase likely exists at other points within the nanowire sample or may exist as completely separated particles.

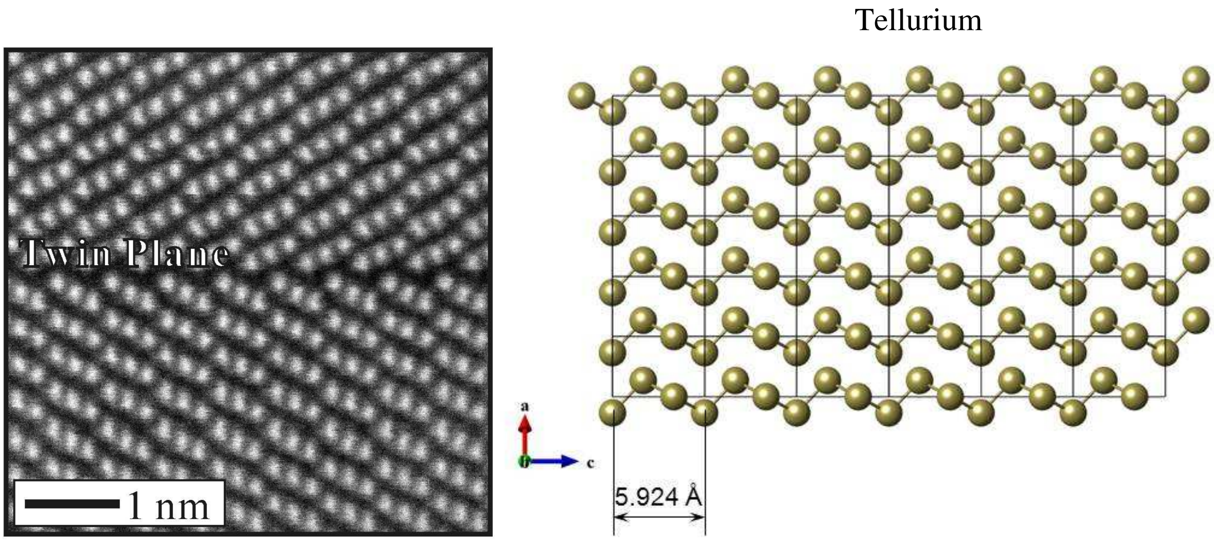


Figure 2: A STEM-HAADF image of a nanowire synthesized with OAM/OAC. The accompanying scheme illustrates the hexagonal structure of tellurium (as viewed across the c-axis).

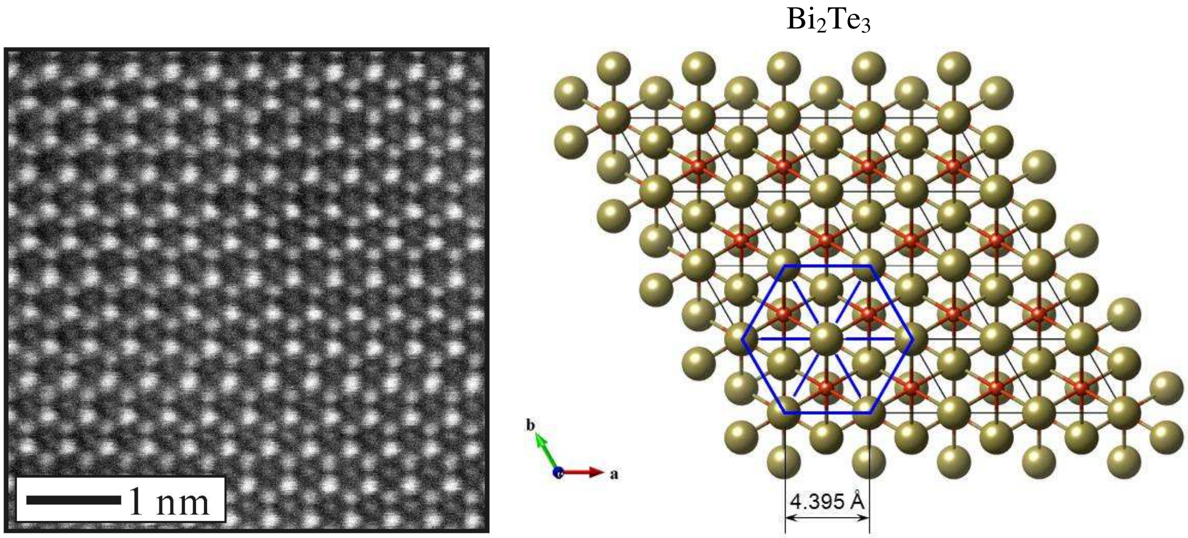


Figure 3: A STEM-HAADF image of a nanodisc on face synthesized with DT. The accompanying scheme illustrates the corresponding rhombohedral structure of Bi_2Te_3 (as viewed down the c-axis).

Figure 3 shows a STEM-HAADF image of a nanodisc on face in roughly the center of the particle. As can be observed, the atomic image appears much different than that for the nanowires. In this image, an alternating pattern of bright, intermediate, and dim atoms can be observed. While this can arise as a result of the high Z-contrast afforded by the HAADF detector, in this case it is likely caused by the atomic structure of the material. The different contrast in the atoms probably arises because of the different depth of the atomic layers in this sample with the bright atoms on top, the intermediate density atoms in the middle, and the dim atoms in the bottom layer. In contrast to traditional TEM, the STEM-HAADF technique relies on scattering of electrons and so the analysis depth is not very high. The materials structure was identified by measuring the interatomic distances within the sample. By identifying the 101 lattice planes with interlayer spacing of 3.75 Å, and the a-axis value of 4.30 Å it was deduced that the material has a rhombohedral structure which is consistent for Bi_2Te_3 (a-axis value of 4.395 Å), Sb_2Te_3 (a-axis value of 4.264 Å) and $(Bi_{0.5}Sb_{0.5})_2Te_3$ (a-axis value of 4.331Å) [6]. The accompanying scheme in Fig. 3 illustrates the rhombohedral structure of Bi_2Te_3 along with the corresponding a-axis value (Sb_2Te_3 and $(Bi_{0.5}Sb_{0.5})_2Te_3$ are also rhombohedral with a similar inter-atomic spacing). This is consistent with the results obtained previously where the nanodiscs were found to be composed of Bi_2Te_3 and Sb_2Te_3 phases [5].

CONCLUSIONS

In conclusion nanoparticles composed of bismuth, antimony and tellurium with both wire and disc shapes were analyzed using scanning transmission electron microscopy coupled with a high angle annular dark field detector. The achievement of atomic level resolution allowed the atomic structure for the particles to be studied. The nanowires were found to be primarily composed of hexagonal phase tellurium while the nanodiscs show a rhombohedral phase consistent with Bi_2Te_3, Sb_2Te_3 or $(Bi_{0.5}Sb_{0.5})_2Te_3$. These preliminary results elucidate the atomic structure of the nanoparticles and are expected to lead to an enhanced understanding for the correlation of the unique properties of nanoparticles and the nanoscale dependent atomic structure.

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