Synthesis and Properties of Bismuth Nanocrystals

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Abstract

We present results of our investigation of the synthesis and structural properties of bismuth nanoparticles. Particles of bismuth with sizes on the order of 10-30 nm are synthesized by low-temperature, solution-chemical techniques. Chemical reduction of bismuth salts takes place in specifically-tailored, aqueous-organic microemulsions. The resulting nanoparticles are characterized by x-ray diffraction, optical absorption and electron microscopy.

Introduction

High efficiency thermoelectric materials depend on the often conflicting requirements of high Seebeck coefficient, high electrical conductivity and low thermal conductivity. Hicks and Dresselhaus [1,2] first suggested that nanometer-scale material structures may provide a way to increase the thermoelectric efficiency. In a nanometer-sized material, the physical dimensions approach the mean-free-path of a carrier (electron or hole). This "quantum confinement" of the carriers can have a profound effect on the electronic and thermal properties of the material. Of interest in thermoelectrics is the increase of the Seebeck coefficient due to altered electronic density of states (relative to bulk) and the lowering of the lattice contribution to the thermal conductivity due to selective phonon scattering and phonon confinement. Indeed, two-dimensional systems, quantum wells and superlattices, have already shown improvement[3] in the thermolectric figure of merit and one-dimensional systems, quantum wires, are currently being studied.[4]

Our goal is to take advantage of the recent advances in the synthesis of nanometer-sized metals and semiconductors, originally developed for optical applications, and investigate the thermoelectric potential of densely-packed "colloidal crystals" composed of random and ordered nanoparticle arrays. Nanoparticles in specific solutions (and under the proper temperature and pressure conditions) will naturally condense into ordered arrays. Thin films and colloidal crystals have been produced in a variety of systems, most notably, CdSe[5] and Au[6-8]. The keys to creating a material structure of this form are highly crystalline, (nearly) monodisperse nanometer-sized particles passivated with a monolayer of organic molecules. The passivation is required so the particles can be dissolved and manipulated in solution and precipitated by evaporation of the solvent. Most importantly, though, the passivation prevents agglomeration of the particles. In this paper, we report our results on the synthesis and physical properties of Bi semimetal nanoparticles synthesized by chemical techniques.

Experiment

Bismuth nanoparticles were chemically synthesized from the reduction of Bi salts in inverse micelles (water-in-oil inverse microemulsions). The bismuth precursor, either bismuth nitrate $Bi(NO_3)_3$ or bismuth citrate $BiC_6H_5O_7$ was dissolved in water and added to the two-component organic solvent mixture to form a microemulsion. This stable microemulsion contains nanometer-sized water droplets containing the dissolved Bi salt. A reducing agent, sodium borohydride, is mixed in a similar microemulsion and added to the Bi salt microemulsion. The chemical reduction to metallic Bi and subsequent particle growth takes place inside the water droplets. To limit oxidation of the fine Bi particles and prevent agglomeration, a polymer component is added. In one procedure, monomer precursors of poly(methyl methacrylate) (PMMA) were added to the oil phase of the microemulsion and polymerized in-situ resulting in a polymeric network which surrounds and protects the Bi nanoparticles. In another procedure, polyvinyl pyrrolidone (PVP) is simply dissolved in the organic solvent used in the microemulsion. When the organic solvents are evaporated under vacuum at room temperature, the polymer is left to coat the Bi particles. Bismuth nanoparticles were also formed using a similar microemulsion route with no polymer encapsulation. All the procedures were performed in a argon atmosphere. Additional details of the synthesis methods are found in Ref. [9]. Some samples were annealed under flowing $8\%H_2/92\%Ar$ gas mixture in a tube furnace.

The morphology and crystal structure of the crystallites is investigated with JEOL JSM-5410 scanning electron microscope (SEM), JEOL JEM-2010 transmission electron microscope (TEM) and Philips X'pert Systems x-ray diffractometer (XRD). The optical absorption data were measured with a Varian/Cary 5000 UV-Vis-NIR spectrometer.

Results and Discussion

Figure 1 shows the x-ray diffraction spectra of the Bi particles coated with PMMA as a function of annealing temperature. As the annealing temperature is increased, the diffraction peaks become sharper. All the peaks are identified with rhomohedral bismuth; no other peaks are present. The average particle size based on the diffraction peak width increases from 15 nm for the as-prepared sample to 27 nm for the sample annealed at 240°C. Figure 2 shows a TEM image of the Bi particles embedded in PMMA and annealed at 240°C. Figure 2 reveals that the particles are rod-shaped and approximately 20 nm × 5 nm. The discrepancy between the particle sizes from x-ray diffraction and TEM is probably due to the presence of some larger particles; that is, x-ray diffraction will give an average grain size over the entire

sample while TEM can only view a small fraction of the particles. Similar x-ray diffraction results were obtained for the PVP-coated particles shown in Fig. 3. The PVP-coated particles range in size from 5 nm to 20 nm and appear to be spherical. In another study, we synthesized and annealed some uncoated bismuth particles. In this case, we find a large percentage of Bi_2O_3 in the x-ray diffraction data. We conclude that the polymers are effective in protecting the particles against oxidation, especially during post-synthesis annealing.

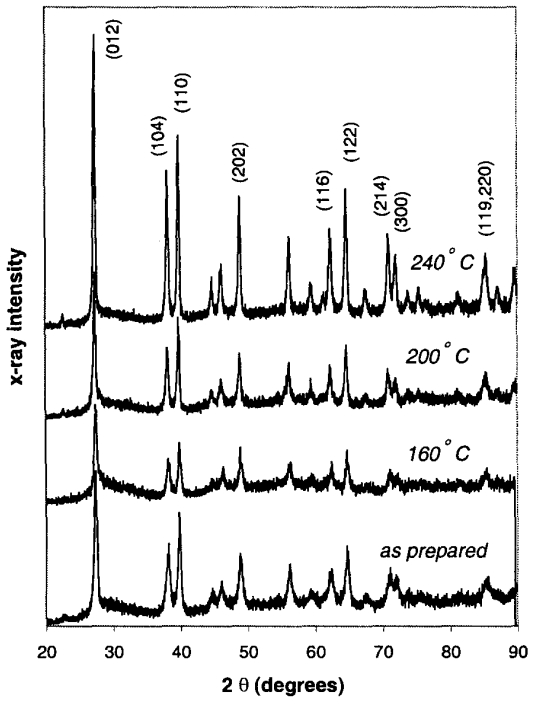

Figure 1. X-ray diffraction of the Bi nanoparticle powder embedded in PMMA polymer. The powder was annealed in 8% H_2/ 92% Ar gas for two hours at the temperatures indicated on the graph. All the peaks can be indexed to rhombohedral bismuth; the main peaks are labeled.

The PMMA-protected particles in a chloroform solution were also characterized by optical absorption. These results are shown in Fig. 4. The prominent absorption feature at ~280 nm is due to the surface plasmon resonance.[10] The surface plasmon resonance is characteristic of nanometer-sized metal particles embedded in a dielectric host and is attributed to a collective oscillation of the electrons in response to optical excitation. This plasmon resonance has not been systematically studied for bismuth particles. However, an absorption peak at 250 nm was reported for Bi particles made by radiolytic reduction[11] and a small, broad feature in the imaginary component of the refractive index at 370 nm was reported for pulsed laser-deposited Bi particles in Al_2O_3.[12]

For a spherical particle, the surface plasmon gives an absorption feature centered at a wavelength, λ, given by[10]

Figure 2. Transmission electron micrograph of Bi nanoparticles embedded in PMMA. This sample was annealed at 240°C.

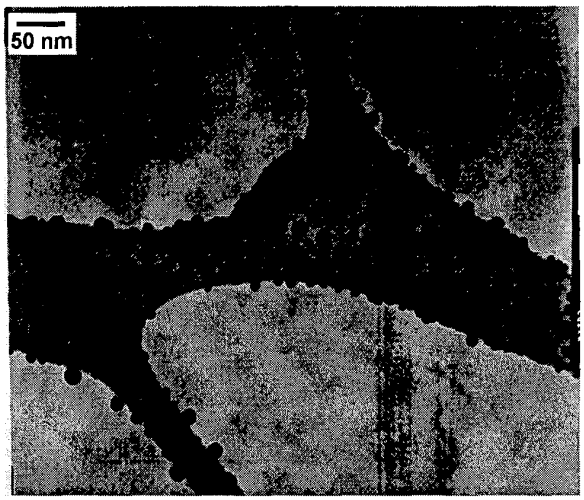

Figure 3. Transmission electron micrograph of Bi nanoparticles coated with PPV

$$\lambda^2 = (2\pi c)^2 \frac{m_0 N e^2}{\varepsilon_0}\left(\varepsilon_\infty + 2n_0^2\right) \qquad (1)$$

where c is the speed of light, m_0 is the carrier mass, N is the carrier concentration, ε_0 is the free-space permeability, ε_∞ is the optical dielectric function of the metal and n_0 is the index of refraction of the host material. Very little data is available for the optical constants of bulk bismuth, but our absorption spectrum seems consistent with the two studies mentioned earlier, Refs. [11] and [12]. Note also that the absorption data in Fig. 4 show two peaks, one at 282 nm and one at 277 nm. We feel that this is a consequence of anisotropic conductivity of bismuth - two different values of dc conductivity will yield two distinct plasmon resonances. The electrical conductivity

parallel to the trigonal axis is about 20% larger that the conductivity perpendicular to the trigonal axis for bismuth at room temperature.[13] This is the right order of magnitude to account for the double peak in Fig. 4, but this has yet to be verified.

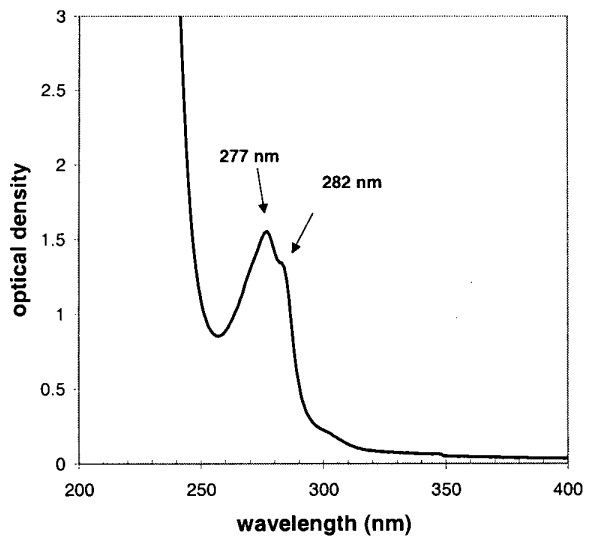

Figure 4. Optical absorption spectrum of Bi nanoparticles dispersed in a PMMA/chloroform solution.

We also attempted to deposit a Bi nanoparticle film onto a quartz substrate using uncoated Bi particles dispersed in toluene. Of course, this solution will have significant particle aggregation so we subjected the solution to ultrasonification and filtered the resulting solution with a 0.2 μm filter. In order to improve adhesion of the particles to the quartz substrate, the substrate was funcionalized similar to the procedure used for fabricating thin films from Au nanoparticles.[6-8] In this procedure, the quartz (SiO_2) substrate is cleaned in a solution of 1:3 H_2SO_4:H_2O_2, rinsed and dried. This leaves the SiO_2 surface terminated with OH groups. The cleaned substrates were then soaked for at least 20 min in 3-(mercaptopropyl) trimethyloxysilane which functionalizes the substrate surface with SH (thiol) groups. After thorough rinsing with toluene, the substrate was then placed into the Bi/toluene colloidal solution (with gentle stirring) and left overnight. Substrates which were cleaned but not subjected to thiol functionalization were also tested. The substrates were removed, rinsed with toluene and dried in a convection oven. The thiol-functionalized substrate was observed to have a gray, thin film while the untreated substrate was almost clear although there was a slight gray area in one corner. An SEM image of the surface of the thiol-functionalized substrate is shown in Fig. 5. Clearly, only a small fraction of the surface contains any material. Some small particles are observed, estimated to be on the order of a few tens of nanometers. Mostly, however, the surface contains particle agglomerates with sizes up to several hundred nanometers. The particle coverage on the untreated substrate was several times worse.

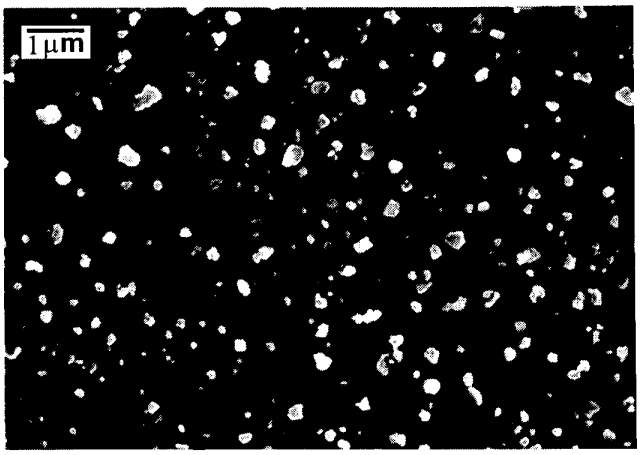

Figure 5. Scanning electron micrograph of Bi particles deposited on a thiol-functionalized quartz substrate.

Conclusions

Nanometer-sized particles of bismuth have been synthesized by chemical methods. X-ray diffraction data show that the resulting powders are highly crysalline with the bulk bismuth (rhombohedral) crystal structure. We found that the introduction of the polymers (PMMA or PVP) into the synthesis procedure protected the Bi particles from oxidation and prevented aggregation. A stable colloidal nanoparticle solution can be obtained in this way. Optical aborption spectra of the stable nanoparticle colloids show a prominent surface plasmon absorption feature at ~280 nm. However, this material was not useful for creating an electrically conductive film. Initial attempts at fabricating a thin film from uncoated bismuth nanoparticles resulted in poor substrate coverage and significant particle agglomeration. Currently we are focussing our research on finding an appropriate organic ligand which will bind tightly to bismuth, passivate the particle surface and facilitate the close-packed assembly of nanoparticle films.

Acknowledgments

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