Pattern Shape-Controlled Self-Assembly of Bi0.90 Si0.10 Nanocrystallites

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ABSTRACT

Nanometer-sized $Bi_{0.90}Sb_{0.10}$ has been, for the first time, prepared using a hightemperature organic solution reducing method. With the presence of proper capping and stabilizing agents, we were able to produce $Bi_{0.90}Sb_{0.10}$ nanoparticles as small as ~12 nm. Nearly monodisperse distributions were obtained through a size-selective post treatment. Transmission electron microscope characterization reveals that the as-prepared particles have a highly crystalline single rhombohedral phase. Self-assembled patterns of $Bi_{0.90}Sb_{0.10}$ were successfully achieved upon evaporation of the solvent from the nanoparticle colloids. As a step toward possible applications of these particles in thermoelectric device structures, we have also demonstrated that we are able to control the pattern of $Bi_{0.90}Sb_{0.10}$ self-assembly from 2D to 1D by employing different solvent systems with varying ratios of polar and non-polar components.

INTRODUCTION

The bulk binary-metal alloy of $Bi_{(1-x)}Sb_x$ can either be a semiconductor or semimetal depending on the composition of Sb [1-3]; pure Bi and Sb are semimetals and $Bi_{(1-x)}Sb_x$ is a semiconductor when $0.07 \le x \le 0.22$. Today, the best thermoelectric materials below 200 K are the bismuth-antimony semiconductor alloys with antimony concentration of approximately 0.12. Hicks and Dresselhaus [4,5] first suggested that nanometer-scale material structures may provide a way to increase the thermoelectric efficiency. It is now well known that a material whose physical dimensions approach the mean-free-path of a carrier (electron or hole) can have a profound effect on the electronic and thermal properties. Actually, two-dimensional systems, quantum wells and superlattices, have already shown improvement in the thermoelectric figure of merit [4,6] and one-dimensional systems, quantum wires, are being investigated [7,8]. Bismuth has often been used for nanometer-scale studies because of its small energy overlap between the conduction and valence bands, high carrier mobilities and small effective masses. Like bismuth, the bismuth-antimony alloys have a highly anisotropic rhombohedral crystal structure and the band structure of BiSb can potentially be engineered by adjusting the particle size and shape in the same manner as Bi. In this work, we present a novel colloidal method for fabricating monodisperse Bi_(1-x)Sb_x nanocrystallites and also demonstrate the capability of controlling the pattern of self-assembled $Bi_{(1-x)}Sb_x$ particles, as a step toward the potential use of these particles in thermoelectric device applications.

EXPERIMENT

Synthesis of $Bi_{(1-x)}Sb_x$ was conducted through a high temperature reduction route in organic solution following an approach similar to our earlier method for preparing pure bismuth nanocrystallites [9]. Bismuth 2-ethylhexanoate (Alfa Aesar) and antimony acetate (SbAc₃, Alfa Aesar, 97%) were used as the precursors. Super-hydride (LiBEt₃H) is used as a reducing agent. LiBEt₃H is commercially supplied in a tetrahydrofuran (THF) solution (Aldrich, 1.0M). Since

THF is a polar solvent and incompatible with our chemical reaction, it must be completely removed and replaced by dioctylether (Aldrich, 99%) under inert gas [10-12].

A typical experiment involved a total solution of ~ 25 ml. Under flowing argon, 0.0180g of SbAc₃, a freshly prepared solution of bismuth 2-ethylhexanoate in dioctylether (0.2M, 1.70 ml) and 0.03 ml of oleic acid (Aldrich, 90%) were added to a three-neck flask that contained 20 ml of degassed dioctylether. The temperature was raised to 100 °C and 0.18 ml of trioctylphosphine (TOP, Aldrich, 90%) was injected into this solution with a syringe while stirring in argon. In order to reduce the precursors at high temperature, the solution was heated to 170 °C, at which point the bismuth-antimony was reduced by injecting 3.0 ml of LiBEt₃Hdioctylether solution (0.5M) (Note: A large amount of gas bubbles may be released). The resulting black solution was maintained at this temperature for 3-5 mins under an argon stream to allow a formation of binary nanocrystals. The flask was then quickly moved into a glovebox and the mixture was subsequently cooled to room temperature. Particles were precipitated by adding a mixture of hexane and ethanol (5: 40 ml) to the system and collected by centrifugation under argon atmosphere. The precipitate was then redispersed into hexane (15 ml) with 2 drops of oleic acid. In order to acquire a self-assembled pattern, the size distribution of the as-prepared colloids must be refined by employing a particle size selection technique[9-13]. Briefly, a polar solvent (ethanol) is added to the hexane colloid causing the largest particles to flocculate, and the mixture is then separated by centrifugation. The smallest particles remain in the supernatant and are recovered.. By repeating this technique, the colloid was separated into several size distributions.

It is worth mentioning that the molar percentage of antimony can be varied from 1% up to 15% in this approach, and the composition ratio of $Bi_{(1-x)}Sb_x$ is adjustable by controlling the molar ratio of bismuth 2-ethylhexanoate to the antimony acetate. For example, with dioctylether as the primary solvent, a 4.0:1.0 molar ratio of bismuth 2-ethylhexanoate to antimony acetate gave $Bi_{0.88}Sb_{0.12}$ particles, a 5.7:1.0 molar ratio produced $Bi_{0.90}Sb_{0.10}$, and a 7.0:1.0 molar ratio yielded $Bi_{0.92}Sb_{0.08}$. The compositions were obtained from energy dispersive x-ray spectroscopy (EDS). The results we are reporting here are based on the sample with ~ 10% mole fraction of Sb.

RESULTS AND DISCUSSION

Nanoparticle Morphology

Figure 1 shows the size distribution of a typical size-selected $Bi_{0.90}Sb_{0.10}$ sample measured by dynamic light scattering (DLS). This light scattering result indicates that the mean hydrodynamic radius of these colloids was ~10.6 nm with a standard deviation of 5.6%. The actual radius of the inorganic nanoparticles was ~6 nm as determined from the transmission electron microscope (TEM) images; the discrepancy is due to the fact that the DLS measurement technique measures hydrodynamic radius which includes both the inorganic particle plus the attached organic molecules. The phase identification of as-prepared $Bi_{0.90}Sb_{0.10}$ was performed at room temperature using (Cu K α radiation) X-ray diffractometer (Philips X'pert System), and confirmed by the TEM diffraction pattern as shown in Figures 2 and 3 (a). We have carefully compared these patterns from XRD and TEM with the standard ICDD PDF Card of Bi (35-0519) and that of $Bi_{0.105}Sb_{0.883}$ (35-0517). This data indicates that our product is highly crystalline with a single rhombohedral phase. In addition, the average crystalline size of this sample was estimated as ~13.0 nm in diameter based on the width of the (012), (104) and (110) peaks [14].



Figure 1. Particle size distribution of $Bi_{0.90}Sb_{0.10}$ nanoparticles derived via the high temperature organic reduction route.





Figure 2. XRD trace of the Bi_{0.90}Sb_{0.10} nanoparticles. The sample was deposited onto a silicon wafer inside a glovebox and protected with polyvinylpyrrolidone.



Figure 3. TEM images of Bi_{0.90}Sb_{0.10} nanocrystallites. (a) diffraction of particle pattern (left); (b) HRTEM of a selected particle (right).

Nanoparticle Assembly

Colloidal particles in solvent are always subjected to Brownian motion with frequent collisions between them. When attractive forces dominate, the particles will aggregate and the dispersion will destabilize; when repulsive forces dominate, the system will remain a stable colloid. Many types of particle-particle interaction forces may exist in a colloidal system. In an organic colloidal system, the most important are the attractive van der Waals forces, and the much shorter range steric repulsive forces arising from the tails of the organic capping ligand. In the process of a self-assembly, however, short-range hydration and solvation forces, which exist on the interface between particles and solvent due to the phase-separation and the packing ordering of molecules [15,16], may also play a dominative role in the "force-balance." In other words, using different types of self-assembly solvents will control the shape of the assembly pattern. The presence of a polar solvent markedly affects the suspension stability in organic media, depending on the polarity, boiling point and concentration of solvent. In this work, we selected two groups of solvents for the self-assembly to investigate (1) how the hetero-atom in a solvent affects the assembly of $Bi_{0.90}Sb_{0.10}$ nanocrystallites and (2) how the solvent polarity affects the shape of Bi_{0.90}Sb_{0.10} self-assembly pattern. In the first group, the size-selected (monodisperse) Bi_{0.90}Sb_{0.10} nanocrystallites were re-dispersed into pyridine, octane, 1-octanol and 1-dodecanethiol with the same concentration. Figure 4 shows the TEM observation of two self-assembled patterns, indicating that octane, a non-polar hydrocarbon solvent, is an excellent

solvent for the self-assembly process, although we found a self-assembly pattern can also be observed by using 1-octanol (polar alcohol). On the other hand, pyridine, an N-containing solvent, may partially react with Bi-Sb nanoparticles since very small clusters (dots) around the assembled particles can be detected (Figure 4a). Additionally, it was found that 1-dodecanethiol is not a good self-assembly medium for Bi-Sb nanoparticles, probably because of the strong reaction between sulfur and BiSb. As an evidence of this conclusion, we observed no patterns from the colloids with a 1-dodecanethiol solvent.



Figure 4. TEM images of self-assembled Bi_{0.90}Sb_{0.10} nanocrystallites using (a) pyridine (left) and (b) octane as solvents (right).

In the second group, we dispersed in the nanoparticles in hexane, octane, 95wt% hexane+5wt% 1-hexanol, 95wt% octane+5wt% 1-octanol and 20wt% isopropanol+80wt% octane to investigate the influence of solvent polarity and nanoparticle concentration. As shown in Figure 5, self-assembly of Bi_{0.90}Sb_{0.10} nanocrystallites takes place when pure hexane was employed as the solvent. However, the shape of assembled pattern is dependent on the concentration of particles. For example, at low concentration, the particles can only "connect" to each other in one dimensional lines, while close-packed two dimensional arrays can be obtained with a reasonably high nanoparticle concentration (Figure 5).



Figure 5. TEM image of self-assembled Bi_{0.90}Sb_{0.10} nanocrystallites using hexane as a solvent. The dispersed particles was maintained in a reasonable high concentration.

To increase the polarity of solvent we combined the hydrocarbon solvent with a miscible alcohol, for example, 95wt% hexane+5wt% 1-hexanol. The resulting patterns are demonstrated in Figure 6, indicating that the self-assembly pattern tends to form a linear shape (1D) rather than a 2D close-packed array. Further, with pure octane as the solvent, the nanoparticles form a 2D close-packed assembly, similar to that from hexane. Of course, nanoparticles deposited from a

higher concentration will form a multi-layer pattern. In addition, by comparing the octane patterns with those of hexane, it reveals that the nanoparticles deposited from the octane colloid are more closely packed, indicating that the pattern of the assembly is also dependent on the evaporation rate of the solvent.



Figure 6. TEM image of self-assembled Bi_{0.90}Sb_{0.10} nanocrystallites using a solvent mixture of 95wt% hexane+5wt% 1-hexanol.



Figure 7. TEM image of self-assembled Bi_{0.90}Sb_{0.10} nanocrystallites using octane as solvent. The dispersed particles was maintained in a reasonably high concentration.

When 5wt% of the octane was replaced by 1-octanol, we could observe an assembled pattern with a wire-like shape (Figure 8), which is similar to that from 95wt% hexane+5wt% 1-hexanol system. The difference is that the width of "wire" increases to about 4-5 nanoparticles wide, as shown in Figure 8. In order to increase the polarity of solvent, we have conducted another experiment using 20wt% isopropanol+80wt% octane. As shown in Figure 9, we obtain linear patterns of disconnected "islands" rather than a continuous band of nanoparticles as with the 95wt% octane+5wt% 1-octanol.



Figure 8. TEM image of self-assembled Bi_{0.90}Sb_{0.10} nanocrystallites using a mixture of 95wt% octane+5wt% 1-octanol.



Figure 9. TEM image of self-assembled Bi_{0.90}Sb_{0.10} nanocrystallites using a 20wt% isopropanol+80wt% octane mixed solvent.

CONCLUSIONS

In conclusion, Bi_{0.90}Sb_{0.10} nanocrystallites have, for the first time, been successfully synthesized through a high temperature reduction in an organic solution with the presence of proper capping/stabilizing agents. The as-prepared Bi_{0.90}Sb_{0.10} exhibits in single rhombohedral phase with high crystallinity. The particle size dispersion in the colloids can be refined with a post treatment size-selection. In addition, the shape of self-assembled patterns of these particles can be varied depending on solvents used in the colloid. According to the results from this work, hetero-atoms (such as S-, N-) containing solvents are not suitable for Bi-Sb nanoparticles because of the possible chemical reactions. Oxygen-containing solvents (long-chain alcohols) may be applicable to this self-assembly system as part of combination solvents. Non-polar hydrocarbon solvents tend to give 2D close-packed assembly patterns, especially in the case of high particle concentration; whilst a combination of non-polar solvent and a polar long-chain alcohol results in a linear, wire-like assembly pattern (1D). Although we can qualitatively explain these assembly processes in terms of general particle-particle and particle-solvent interactions, the detailed mechanism of self-assembly process is very complicated. Further investigation to elucidate the chemistry and physics of these colloidal processes is in progress.

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