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Synthesis of Sub-20-nm-Sized Bismuth 1-D Structures Using Gallium−Bismuth Systems

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Bismuth (Bi) nanowires are interesting one-dimensional systems due to the significant quantum confinement effects exhibited as a function of the wire diameters, and synthesizing Bi nanowires with sizes below 20 nm is of fundamental importance in understanding quantum effects. Here, we report a bulk synthesis method to synthesize ultrafine Bi nanowires and a new morphology of bismuth nanostructures, tapered whiskers. These tapered whiskers are about 10−20 μm in length and have diameters of 5−10 nm at the tip and 250−500 nm at the base. The synthesis method is based upon the multiple nucleation and basal growth of nanometer scale nuclei from molten gallium (Ga) melts that result from the low solubility of Bi in Ga and the low eutectic temperature of the Ga−Bi binary system. Adopting different methods of supplying bismuth and using variations in simple heating and cooling, we have synthesized a variety of bismuth nanostructures.

Bismuth (Bi) is a very unique metal. In the bulk form, Bi is a semimetal having a small effective electron mass, a long carrier mean free path, and an anisotropic Fermi surface. The small electron effective mass of Bi gives rise to more prominent quantum confinement effects than nanowires of other materials. Bi nanowires have been predicted to exhibit distinct quantum confinement effects with the transition from semimetallic to semiconducting behavior as wire diameters decrease.[1] There has been long-standing interest in the properties of Bi for both a fundamental understanding of quantum confinement effects and device applications. One of the most promising applications of bismuth nanowires is in thermoelectric devices.[2] For a material to be a good thermoelectric cooler, the dimensionless thermoelectric figure of merit, ZT, must be high. Increasing the Seebeck coefficient can increase the figure of merit. For bismuth, it has been shown that decreasing wire diameters can result in an increase in the Seebeck coefficient.[3] This provided the impetus to develop synthesis methods for smaller diameter Bi nanowires for thermoelectric applications. In addition, sub-10-nm nanowires provide an ideal system for studying the fundamental transport properties of Bi.

Currently, Bi nanowires are primarily synthesized using template-assisted methods such as electrodeposition, pressure injection, or vapor phase deposition of Bi into porous alumina templates.[4−8] One drawback of template-assisted methods is that the wire diameters are limited by the template pore diameters. In the case of pressure injection, the smallest diameter reported is 65 nm. The smallest diameter reported using vapor phase deposition in templates is about 7 nm.[7] The diameter distribution of the resulting nanowires directly depends on the pore diameters of the templates. Preparing templates with smaller pores is a nontrivial task. Other reported methods for synthesizing Bi nanowires include a solvothermal process,[9] stress-induced growth,[10] and e-beam writing.[11]

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Here, we describe an approach utilizing the bulk nucleation and growth of Bi out of molten gallium (Ga), a quasi-immiscible solvent. Both Bi and Ga are considered low-melting-point metals, but the solubility of Bi in molten Ga is quite low at temperatures below 100 °C. Before discussing the experimental details, it is worthwhile to consider the properties of the Bi−Ga system. Both Bi and Ga are low-melting metals, with Ga melting just above room temperature and Bi melting at 271 °C. At higher temperatures, both Bi and Ga coexist in the liquid phase.[12] It is also known that Bi preferentially segregates on top of liquid Ga−Bi melts.[13−15] Due to its low solubility in Ga, Bi is expected to precipitate out as nanometer scale nuclei from Ga.

This concept of employing bulk nucleation to synthesize nanowires was first described using another similar quasi-immiscible system involving Si as the solute and molten Ga as the solvent.[16] Furthermore, the above concept has been demonstrated with several other systems such as gallium nitride (GaN), gallium oxide (Ga_2O_3), a-SiO_x, and a-Si_xN_yH.[17−19] In all of these cases, the critical aspect is to dissolve the solute in molten Ga using either solid or vapor phase sources with the help of thermal or plasma activation, respectively. Therefore, the goal of this work was to determine whether the concept also applies to metals such as Bi using Ga as the quasi-immiscible solvent and using it to create sub-20-nm-sized Bi nanostructures in large quantities.

Four different sets of synthesis experiments were performed: (a) heating and cooling of Bi−Ga mixtures in a vacuum chamber, (b) heating and cooling of Ga−Bi mixtures in the presence of hydrogen plasma, (c) evaporation of Bi onto Ga films, and (d) coevaporation of both Bi and Ga onto quartz substrates.

The first set of experiments involved heating a Ga−Bi mixture under vacuum above 600 °C for about 1 h and then allowing the system to cool to room temperature. In these experiments, Bi powder was sprinkled on top of Ga films on either graphite or quartz substrates. The weight ratio of Bi to

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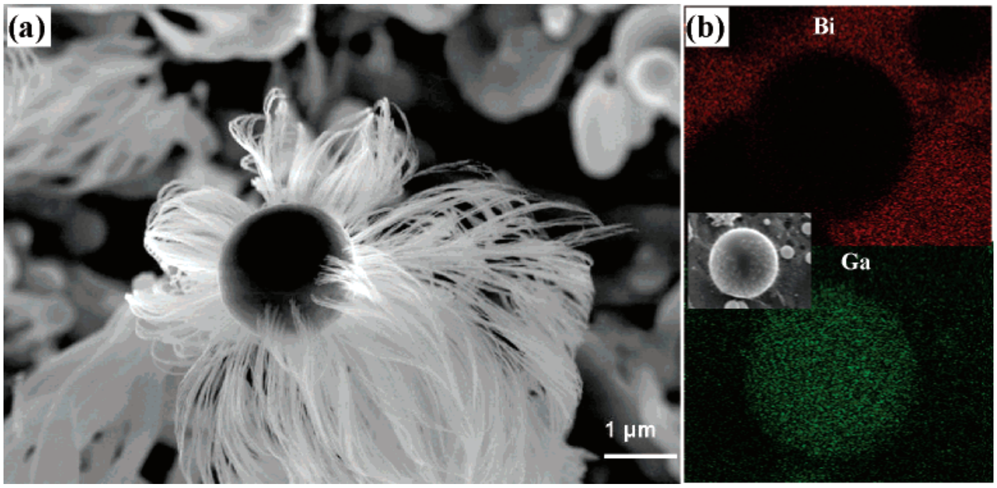

Figure 1. (a) SEM micrograph and (b) EDS elemental mapping illustrating the growth of Bi from Ga droplets in the heating/cooling experiments.

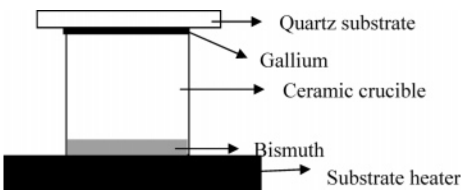

Figure 2. Experimental setup used to supply Bi from the vapor phase onto films of Ga spread on quartz substrates.

Ga was kept at about 1% or less in these experiments. Figure 1 shows the resulting Bi nanowires emanating from Ga droplets in these experiments, clearly illustrating the concept of multiple nucleation and basal growth. As mentioned earlier, both Ga and Bi exist as molten metals at temperatures greater than 300 °C. Therefore, during the 1 h heating period when the system was kept at 600 °C, the mixing of Bi into the Ga solvent occurred to provide Ga supersaturated with Bi. The nucleation and growth of Bi nanowires from Ga occurred during the cooling process. Similar to our earlier results with Si nanowires from Ga, the resulting nanowires have a uniform size distribution within experimentally measured values.

In the second set of experiments, Bi was evaporated onto Ga-covered quartz substrates in a simple setup, as shown in Figure 2. In these experiments, Bi powder was placed in a ceramic crucible heated using a flat, resistive, ceramic-coated heater. Experiments with Bi supplied via vapor phase transport also resulted in Bi nanowires. The Bi nanowires obtained from these experiments are intertangled due to the high density of wires growing out of the Ga, which leads to "braided" morphologies, as shown in Figure 3. These braided morphologies seem to support the Ga droplets while continuing the growth of Bi nanowires for the braids with a continuous supply of Bi from the vapor phase.

Another variation of those experiments involved the simultaneous evaporation of Bi and Ga onto blank quartz substrates. Bi and Ga behaved similarly in these experiments, yielding nanowires in the flower-shaped morphologies shown in Figure 4, which can be explained by the low evaporation rates expected for Ga, thus reducing the sizes of the Ga droplets.

In the coevaporation experiments, a few Bi sheets were also observed, as shown in Figure 5. Due to uneven evaporation rates for Bi and Ga, the excess Bi precipitated out to the top of the Ga surface, forming sheets.

Another type of heating experiment was performed employing microwave (MW) generated hydrogen (H_2) plasmas, as shown in Figure 6. A graphite substrate (0.5-in. diameter) covered with Ga and Bi was placed on a larger graphite support disk (2-in. diameter). The H_2 plasma conditions were a reactor pressure of 40−100 Torr and a MW power of 1100 W for 1 h. Under these conditions, the temperature of the substrates reaches about 750 °C or more. Therefore, upon turning off the MW power and allowing the system to cool to room temperature, it was expected that Bi nanowires would form similarly to those shown in Figure 1. However, these experiments resulted in a new morphology for bismuth nanostructures, that is, in the form of tapered nanowhiskers with tip diameters less than 5 nm and base diameters of about 200−500 nm, as shown in Figure 7. The tapered whiskers grow out of Ga−Bi droplets at the base, as indicated in Figure 7.

The tapered whiskers were primarily formed on the larger graphite support disk with very few whiskers on the actual substrate area, indicating the vapor transport of Bi and Ga. Due to inherent plasma nonuniformity in our system beyond a 1-in. area, the temperature decreases radially with the highest value at the center. During plasma exposure, most of the Ga is

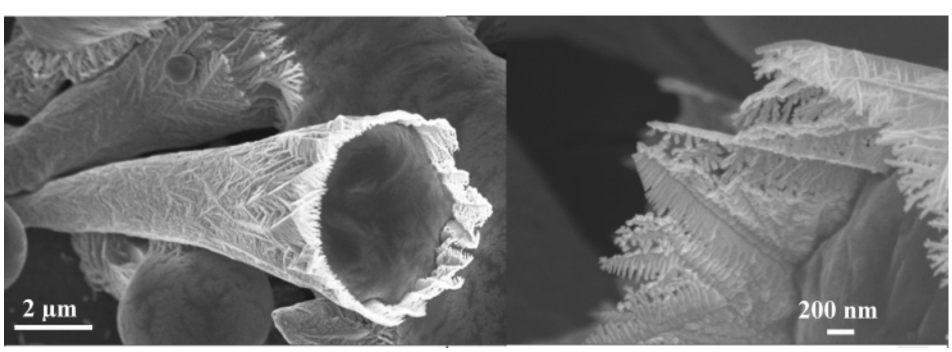

Figure 3. SEM micrographs of braided Bi nanostructures synthesized by evaporating Bi onto a film of Ga.

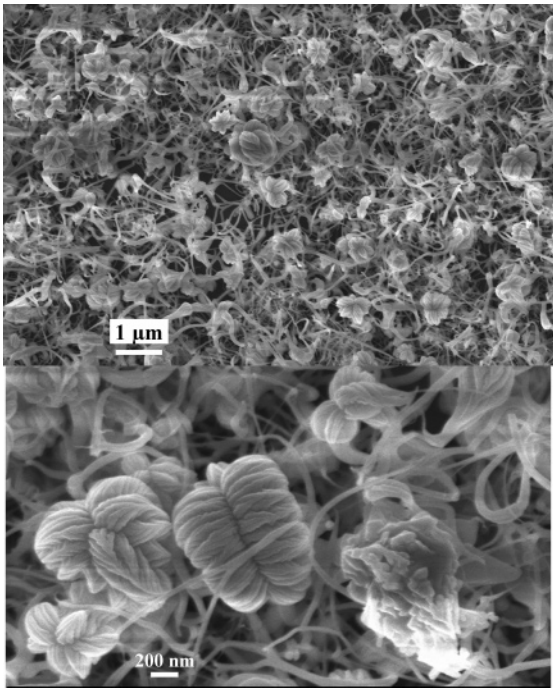

Figure 4. SEM micrographs of Bi nanowires in the flower morphologies.

transported as Ga droplets onto the underlying substrate holder. At the same time, Bi with its higher vapor pressure is transported radially onto the substrate holder. The vapor phase supply of Bi onto Ga in the absence of plasma and lower temperatures resulted in braided morphologies similar to those shown earlier. In the present case, due to higher temperatures, the braided morphologies have reorganized into a solid form, resulting in tapered whiskers. A quartz substrate placed at the edge of the graphite disk holder, where the temperature is lower than the central region, resulted in nanowire growth out of Ga droplets, as shown in Figure 8. MW plasma experiments using a much lower power (between 500 and 600 W) resulted in the formation of Bi nanowires from Ga droplets irrespective of the location on the substrate. No tapered whisker morphologies were observed either. Also, experiments using methane (CH_4) in the feed gases (18−20% CH_4/H_2) and higher MW powers (1100 W) resulted in the formation of tapered whiskers with a protective sheath of carbon on the surface of the whiskers (not shown here).

Results from several variations of heating/cooling experiments involving Ga−Bi systems clearly illustrate the concept of multiple nucleation and basal growth of Bi nanowires from molten Ga. The results also show that sub-10-nm nanowires

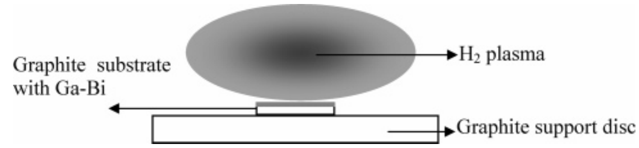

Figure 6. Schematic of the setup used in the plasma enhanced heating experiments.

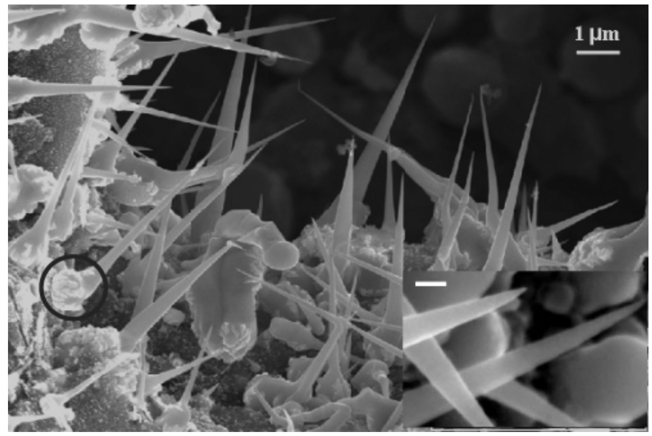

Figure 7. SEM micrographs of tapered Bi nanowhiskers formed during the H_2 plasma exposure of Ga and Bi. The inset illustrates the fine tip of the nanowhiskers (scale bar 40 nm).

can be synthesized. The results from different sets of experiments also indicate that the morphology of Bi nanostructures can be varied from nanowires to nanowhiskers to braided structures by varying the conditions such as solid versus vapor sources and evaporation rates. The results also indicate that any of the experiments can be scaled to larger substrate areas to generate bulk amounts.

High-resolution transmission electron microscopy (TEM) and electron diffraction analysis of Bi nanowires and whiskers indicate that they are essentially single crystalline, as shown in Figure 9. The growth direction is determined to be [003]. The nanowires and the sharper region of the tapered regions were very sensitive to the high-energy electron beam and often “melted” during TEM investigations.

The synthesis procedure illustrated is simple, since it only involves the heating and cooling of a mixture of a solute and a low-melting metal solvent in the presence of hydrogen. The hydrogen atmosphere is expected to keep a high surface tension between low-melting metals (such as Ga, In, Bi, and Zn) to ensure the basal growth of the nanometer scale nuclei resulting from phase segregation into nanowires. Not only is our concept simple, but it can also be easily tested with other solute and low-melting metal solvent systems to produce nanowires of the solutes and their alloys with the low-melting metal solvents.

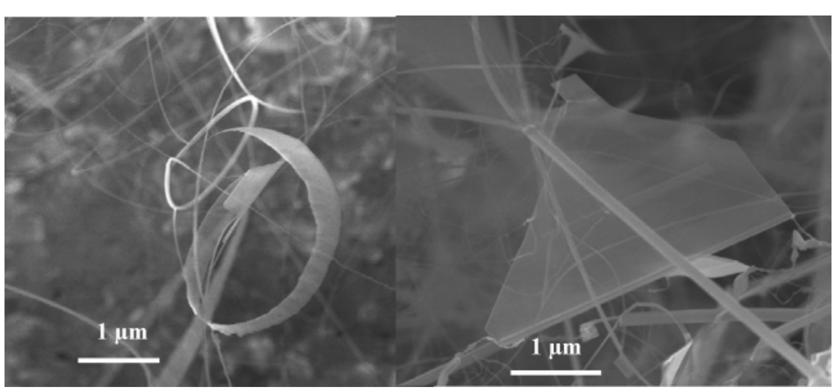

Figure 5. SEM micrographs of Bi sheets observed during the coevaporation experiments.

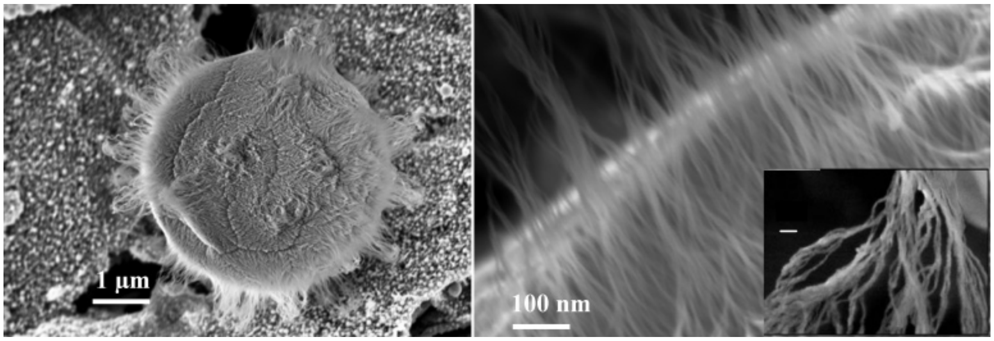

Figure 8. SEM micrographs of bismuth nanowires grown on the quartz sample placed at the edge of the substrate holder. The inset shows a SEM micrograph of bismuth nanowires with diameters less than 10 nm (scale bar 40 nm).

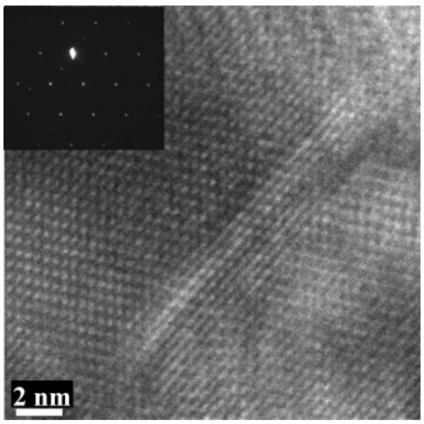

Figure 9. High-resolution TEM image of the Bi whisker with an inset showing the single crystal diffraction pattern.

TABLE 1: Summary of Experimental Conditions and the Resulting Morphologies of the Nanostructures

experimental conditions	resulting morphologies
heating and cooling a mixture of Ga and Bi	nanowires
evaporation of Bi onto a thin film of Ga	braided nanowires
coevaporation of Bi and Ga	flower morphologies and thin sheets
microwave plasma enhanced heating and cooling	tapered whiskers

In summary, we demonstrated the concept of multiple nucleation and basal growth of Bi nanowires using Ga−Bi systems. Two primary approaches, involving the heating/cooling of Ga−Bi solids and Bi evaporation onto Ga-covered quartz substrates, resulted in the bulk nucleation and growth of Bi nanowires from Ga droplets. The sizes of the Bi nanowires were approximately 5−10 nm in diameter and a few microns in length. By varying the temperature and supply of Bi, various morphologies of Bi nanostructures were obtained: nanowires, braided morphologies, and tapered whiskers, as summarized in Table 1. The techniques utilized in the experiments are simple and scalable for the bulk quantity production of sub-10-nm Bi nanowires using Ga thin films over large substrates. Our concept may have a wide-ranging applicability to other solute and low-melting metal solvent systems for bulk nanowire synthesis as well.

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Supporting Information Available: Higher magnification SEM micrograph of bismuth nanowires growing out of gallium droplets, comparison of secondary electron image and back-scattered image of bismuth nanowires growing out of gallium droplets, low-magnification SEM image of tapered whiskers illustrating growth over larger areas, and scanning transmission electron microscopy (STEM) line profile elemental analysis indicating a protective carbon sheath around the tapered whisker. This material is available free of charge via the Internet at http://pubs.acs.org.

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