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High Yield Solution−Liquid−Solid Synthesis of Germanium Nanowires

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Here we report the high yield solution−liquid−solid synthesis of crystalline Ge nanowires. Bi nanocrystals are used as seeds to promote nanowire growth in trioctylphosphine (TOP) from decomposing GeI_2 at ∼350 °C. This is the first example of a group IV nanowire synthesis in a conventional solvent under atmospheric pressure.

Research in semiconductor nanowires has been fueled by their unique optical, electronic, and mechanical properties and their potential use in optoelectronic devices, chemical and biological sensors, computing devices, and photovoltaics.[1] Semiconductor nanowires have been synthesized under a wide range of conditions, from high temperature (<1100 °C) gas-phase reactions[1,2] to relatively low temperature (>250 °C) solution-phase conditions.[1,3−5] Solution-phase routes to semiconductor nanowires are particularly interesting due to their potential for good size and shape control, chemical surface passivation, colloidal dispersibility, and high throughput continuous processes.

Nanocrystals and nanowires of group IV materials, such as C, Si, and Ge, have been extremely challenging to synthesize in solution due to their high crystallization energy barrier and the propensity of those elements to form stable oligomeric species with hydrocarbons. In the past, our approach to crystalline Si[6] and Ge nanowires[7] and multiwall carbon nanotubes[8] has been to use supercritical solvents that are heated well above their boiling points to temperatures between 350 and 650 °C by pressurization. These temperatures exceed the decomposition temperatures of organosilane and organogermane precursors and the Au:Si and Au:Ge eutectic temperatures (∼360 °C), making it possible to promote Au nanocrystal-seeded nanowire growth.[9] Although very high quality nanowires are obtained, it would be more desirable to synthesize crystalline nanowires under milder conditions to alleviate solvent decomposition and safety concerns.

The low melting metal, Bi, forms a eutectic with Ge at 271.4 °C (Scheme 1),[10] which is well within the temperature window for conventional solvents. Buhro[4] first showed that Bi nanocrystals could seed SLS growth of CdSe nanowires, which Fanfair and Korgel[5] later extended to group III−V nanowire synthesis. On the basis of the Bi:Ge phase diagram, Bi is also a good candidate for Ge nanowire synthesis. Ge nanowire synthesis in a conventional solvent also requires a precursor that is sufficiently reactive at ∼350 °C. We recently identified GeI_2 as an effective precursor for Ge nanocrystal synthesis at 300 °C in TOP, with high yields and minimal organic contamination.[11]

Scheme 1. Binary Phase Diagram of Ge−Bi and Ge Nanowire Growth Mechanism

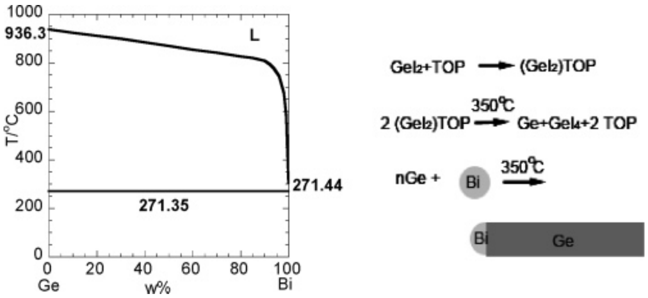

Figure 1 shows Ge nanowires produced by injecting GeI_2 along with sterically stabilized 20 nm diameter Bi nanocrystals into TOP at 365 °C on a Schlenk line (see Supporting Information for details). The Bi nanocrystals were synthesized by room temperature reduction of bismuth(III) 2-ethylhexanoate ($Bi[OOCCH-(C_2H_5)C_4H_9]_3$) in dioctyl ether in the presence of TOP as described in ref 5. TOP serves as a capping ligand that prevents significant nanocrystal aggregation but does not interfere with nanowire growth. After injecting the precursor/nanocrystal mixture swiftly into preheated TOP at 365 °C, the reaction vessel was stirred for 10 min at 350 °C. The resulting black precipitate of nanowires was washed with toluene, chloroform, and ethanol. The best Ge nanowire product was obtained using a GeI_2:Bi mole ratio of 80:1. Scanning electron microscopy (SEM) of the reaction product synthesized from GeI_2 and Bi nanoparticles in TOP at 350 °C showed a large amount of nanowires (Figure 1). The wires were long and generally straight, ranging in diameter from 20 to 150 nm with an average of ∼50 nm, with aspect ratios exceeding 100. The average length of the nanowires is greater than 5 μm, and many are longer than 10 μm. The relatively broad diameter distribution is primarily the result of the Bi nanocrystals used to seed the reaction—although the Bi nanocrystals were relatively size-monodisperse to begin with, Bi nanocrystals are notoriously difficult to stabilize and aggregate quickly during the nanowire synthesis, leading to a broad nanowire diameter distribution. The product was nearly free of contaminants,

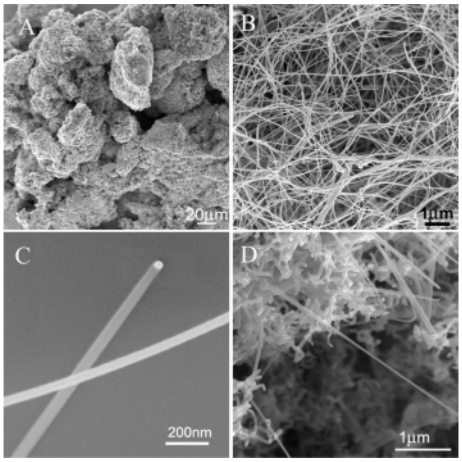

Figure 1. (A−C) SEM images of Ge nanowires made from GeI_2 in TOP at 350 °C with Bi nanocrystals as growth seeds (GeI_2:Bi = 80:1 n:n). SEM reveals a high yield of high quality Ge nanowires with an average diameter of 50 nm. (C) A representative Ge nanowire shows a Bi nanoparticle at its tip. (D) Ge nanowires synthesized at a lower mole ratio of GeI_2 to Bi of 50:1 (n:n) were of lower quality.

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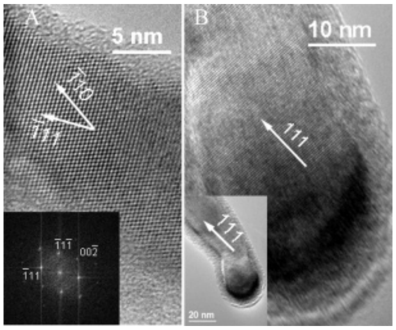

Figure 2. High-resolution TEM images of the Ge nanowires. (A) A 15 nm nanowire with ⟨111⟩ growth direction. (Inset) FFT indicates the nanowire was imaged down the [1$\bar{1}$0] zone axis. The forbidden spot of [00$\bar{2}$] is from double diffraction of [$\bar{1}$1$\bar{1}$] and [1$\bar{1}\bar{1}$]. (B) Ge nanowire with a tip showing presence of Bi by EDS analysis. (Inset) A lower magnification TEM image of the wire with ⟨111⟩ growth direction.

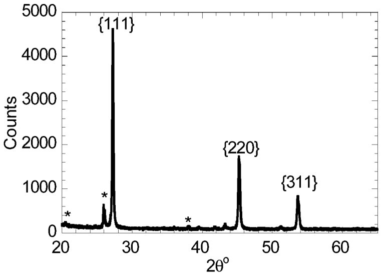

Figure 3. XRD of Ge nanowire shows diamond cubic crystal structure of Ge with {111}, {220}, and {311} peaks. The peaks labeled with * are from hexagonal GeO_2.

and the Ge nanowire reaction yield is very high: 7.5 mg of pure Ge nanowires was obtained in a typical reaction with 0.6 mg of Bi nanoparticles and 75 mg of GeI_2 in 5 mL of TOP, corresponding to a yield of ∼40%. Bi particles could be observed at the ends of some Ge nanowires, as shown in Figure 1C. Energy-dispersive X-ray spectroscopy (EDS) mapping confirmed that the particles are composed of Bi (SI-2). At a lower GeI_2:Bi ratio (GeI_2:Bi = 50:1), both straight and tortuous wires were observed (Figure 1D)—the tortuous wires have a similar average diameter but shorter length (<1 μm).

High-resolution transmission electron microscopy (HRTEM) (Figure 2) and X-ray diffraction (XRD) (Figure 3) both confirmed that the nanowires were crystalline diamond cubic Ge. Figure 2 shows two nanowires imaged by TEM: the nanowire growth direction was predominantly ⟨111⟩, as seen here. A small number of nanowires (∼10% of the sample) exhibited ⟨110⟩ growth direction (SI-1). A mixture of ⟨111⟩ and ⟨110⟩ growth direction is similar to what has been observed for Ge nanowires synthesized in supercritical solvents.[7,12] The straight Ge nanowires are single crystals, nearly free of extended defects. The XRD pattern in Figure 3 exhibits diffraction peaks corresponding to the {111}, {220}, and {311} reflections of diamond cubic Ge. A small amount of GeO_2 can also be observed in the XRD pattern, which is consistent with TEM images that showed the nanowire surfaces to be oxidized.

Scheme 1 outlines the nanowire growth mechanism. Two key aspects of the chemistry enable the production of crystalline Ge nanowires in TOP: (1) the low temperature Bi:Ge eutectic at ∼270 °C, and (2) the highly reactive organic-free Ge precursor, GeI_2. GeI_2 disproportionates to Ge and GeI_4 with relatively high chemical yield at temperatures greater than ∼330 °C—far below its boiling point at 550 °C and the boiling point of many widely used solvents, such as tri-*n*-octylphosphine (TOP). GeI_2 also forms a very soluble complex of $(GeI_2)\cdot R_3P$,[13] when mixed with TOP, which dissociates at 120 °C, making it an ideal precursor for SLS Ge nanowire synthesis. Control experiments where GeI_2 was injected without Bi nanocrystals into TOP at 365 °C showed Ge nanoparticle formation in just 5 min, indicating rapid homogeneous GeI_2 decomposition. With Bi present in the concentrations used for nanowire synthesis, Ge nanoparticles were not observed. Although small Ge clusters may nucleate homogeneously, their interfacial free energy is greatly lowered by incorporation into the much larger 20 nm Bi particles. Heterogeneous GeI_2 decomposition on the Bi seed particle surface could also occur.

It should be possible to extend the approach to Si, as Bi:Si also has a eutectic temperature at ∼270 °C. The key to Si nanowire synthesis will be the identification of a suitable reaction pathway to produce a high yield of Si from molecular precursors at temperatures below 350 °C. In addition to Bi, other low melting metals, such as In (156 °C)[3] and Sn (231 °C),[14] form liquid alloys with Ge/Si at mild temperatures, making them promising candidates for group IV nanowire growth seeds, as well.

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Supporting Information Available: Synthesis details, HRTEM image showing ⟨110⟩ growth direction of a Ge nanowire, and EDS of a Ge nanowire with Bi tip. This material is available free of charge via the Internet at http://pubs.acs.org.

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