Bismuth-Catalyzed Growth of Germanium Nanowires in Vapor Phase

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We report the successful synthesis of single crystalline Ge nanowires using Bi as catalyst. To the best of our knowledge, this is the first time Bi was used in vapor phase for Ge nanowire growth. An in situ catalyst evaporation method was used to obtain the high quality Ge nanowires. Diameters of the nanowires are in the range of 10−40 nm and the growth direction is along <111>. Composition analyses showed that the nanowires were composed of Ge while the capping catalyst particles were Bi. Controlled experiments showed that source material with proper Bi/Ge molar ratio was a key aspect for the growth of high purity nanowires. The low-temperature growth of Ge nanowires, enabled by the low eutectic point of Bi/Ge, is especially desired for their potential integration with existing semiconductor technologies.

Introduction

Semiconductor nanowires have attracted much attention because of their potential use as building blocks for future nanoscale devices.[1−3] Among them, Ge nanowires are of particular interest for high performance nanoelectronic devices due to the high carrier mobility.[4−8] Direct integration of nanowires into well-established semiconductor-processing technology has been achieved for the fabrication of nanowire-based transistors.[9,10]

The majority of the research in Ge nanowire synthesis is based on the vapor−liquid−solid (VLS) mechanism.[11] During the nanowire growth, a metal catalyst particle forms a eutectic liquid alloy with Ge at the growth temperature. The liquid droplet readily supersaturates and precipitation of solid Ge leads to axial nanowire growth. Until now, Au is the dominant catalyst metal used for semiconductor nanowire synthesis, due to its chemical inertness, thermal stability, and ability to form a eutectic alloy at low temperature.[12] However, Au has been found to diffuse into the semiconductor nanowires during growth.[13] The metal−catalyst contamination of Au is a long-standing concern because Au is highly detrimental to the performance of minority carrier electronic devices.[13−15] Thus, it is critical to develop suitable alternative metal catalysts to advance nanowire-based device technologies. Efforts have been focused on seeking nongold catalysts for semiconductor nanowire seeding. Alternative metal catalysts for semiconductor nanowire seeding have been reported, such as Al,[16] Mn,[17] In,[18] and several metal compounds.[19] Especially, Bi was employed to catalyze the growth of several groups of semiconductor nanowires in solution phase.[20−23] However, to the best of our knowledge, the growth of Ge nanowires in vapor phase using Bi as metal catalysts has not been investigated.

In this paper, we present the synthesis of high quality single-crystalline Ge nanowires using Bi as the catalysts via an in situ catalyst evaporation method. Detailed morphology, structure, and chemical composition analyses of the nanowires are presented. Controlled experiments aiming for high purity Ge nanowire synthesis and growth mechanisms of the nanowires are discussed.

Experimental Section

The synthesis of Ge nanowires was based on a high-temperature horizontal quartz tube furnace system. Mixed bismuth, germanium, and carbon powders (molar ratio Bi:Ge:C = 0.05:1:1) were loaded at the center of the furnace. The central temperature was increased to 1000 °C at a rate of 10 °C min^{-1} and kept for 60 min under a constant Ar flow of 200 sccm (standard cubic centimeter per minute). Copper grids coated with holey carbon film were placed at the lower temperature region (around 300 °C) to collect the products. The ambient pressure inside the tube was around 1 Torr during the growth process. Subsequently, the furnace was cooled to room temperature. The morphology and structure of the products were characterized by field emission scanning electron microscopy (FESEM, JEOL 6340F) and transmission electron microscopy (TEM, JEOL 2010). No further treatment was needed since the nanowires were grown directly on the copper grids. The chemical compositions were analyzed using energy dispersive spectroscopy (EDS) attached to the TEM system.

Results and Discussions

Typical low magnification TEM images of the Ge nanowires are shown in Figure 1, panels a and b. Large quantities of nanowires can be observed, with diameters in the range of 10−40 nm. High magnification TEM images are shown in Figure 1, panels c and d. Metal catalyst particles can be clearly observed at the growth fronts (dark spots), indicating that the nanowires were synthesized via the VLS mechanism.[11]

A lattice-resolved high-resolution transmission electron microscopy (HRTEM) image of the Ge nanowire taken along the [101] zone axis is shown in Figure 2. The corresponding two-dimensional fast Fourier transform (FFT) is shown in the inset, which indicates that the growth direction of the nanowire is along the <111> direction. A measured lattice spacing of 0.326

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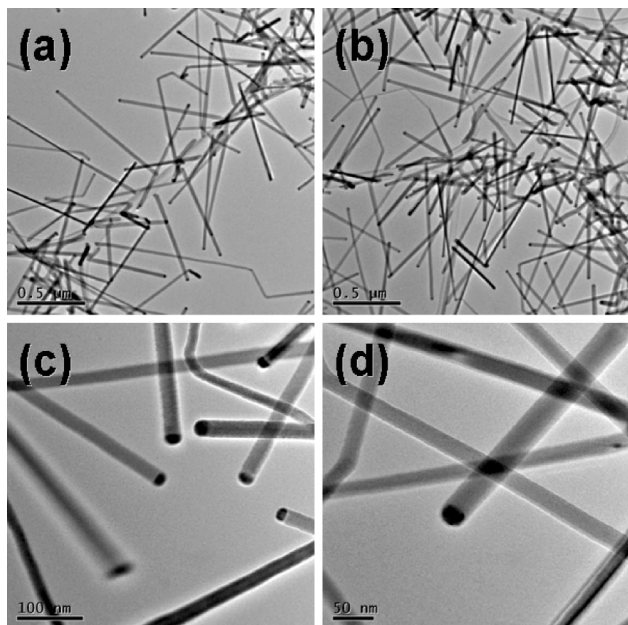*J. Phys. Chem. C, Vol. 113, No. 6, 2009* **2209**

Figure 1. (a and b) Low magnification TEM images of the Ge nanowires; (c and d) representative high magnification TEM images show metal catalyst particles at the growth fronts.
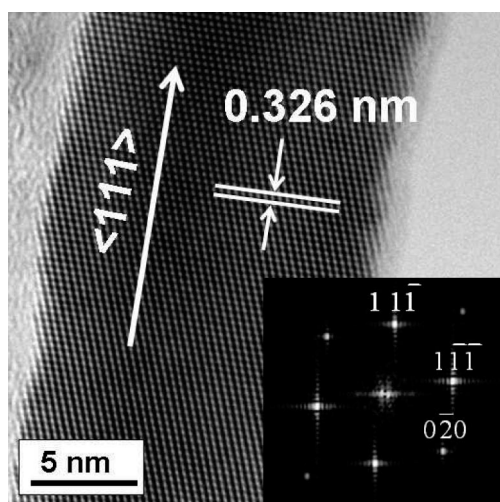

Figure 2. HRTEM image of the Ge nanowire growing along <111> direction. Inset is the corresponding two-dimensional Fourier transform along the zone axis of [101].

Figure 3. (a) EDS spectrum taken from a collection of nanowires; (b) EDS line-scanning profile across a metal catalyst particle, showing that the catalyst particle and nanowire are composed of Bi and Ge, respectively. Inset is the corresponding scanning TEM (STEM) image of the nanowire with catalyst particle. White line denotes the scanning path for EDS analysis.

nm corresponds to the spacing between {111} planes of the diamond crystal structure of Ge (JCPDS 4−0545: $a = 5.6576$ Å). All of the nanowires characterized were found to grow along the <111> direction, with no other growth directions being observed. It is also reported that the predominant growth direction for Ge nanowires synthesized in solution phase using Bi as catalysts is <111>.[23]

Compositions of the nanowires and catalyst particles were analyzed using EDS in the TEM system. Apart from Ge, a small Bi peak was also detected, as shown in Figure 3a. Peaks of Cu come from the Cu grid used for TEM characterization. EDS line scanning profile across a catalyst particle is shown in Figure 3b. The scanning result suggests that the catalyst particle and the nanowire are composed of Bi (red line) and Ge (blue line), respectively. This confirms the successful synthesis of Ge nanowires using Bi as metal catalysts. Oxygen element (black line) is absent both from the catalyst particle and the nanowire body.
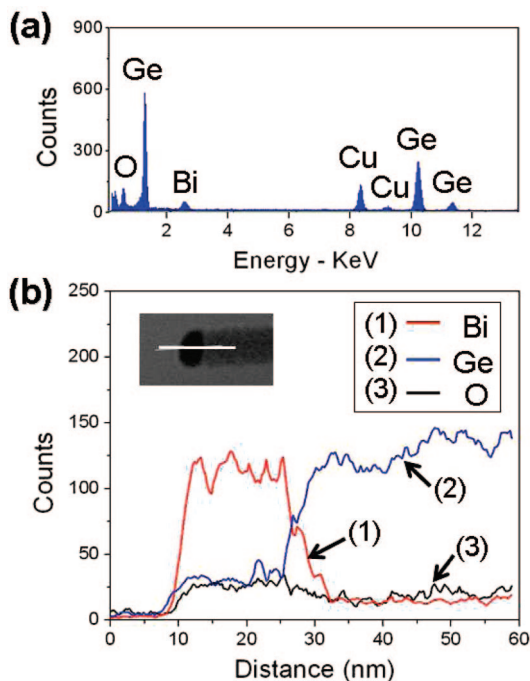
One key aspect that enables the successful synthesis of Ge nanowires is the molar ratio of Bi/Ge in the source materials. The effect of Bi/Ge molar ratio was investigated through controlled experiments using source materials with different Bi contents. Instead of the growth of Ge nanowires, large Bi particles of micrometer-sizes would condense at the low temperature region on the substrate when source materials of high Bi content were used. For typical experiments using source materials with a Bi/Ge molar ratio of 0.2/1, representative FESEM images of the product morphologies are shown in Figure 4, panels a and b. Multistacks of Bi particles condensed on the substrate. The growth of Ge nanowires was significantly inhibited by the large particles or even continuous films.

Both the yield and purity of the nanowires could be improved when source material with a Bi/Ge ratio of 0.05/1 was used (Figure 4, panels c and d). The density of the nanowires started to decrease when the molar ratio was even lower. A proper Bi content (0.05/1 for our case) in the source materials is critical to ensure the formation of small Bi particles with desired densities, which later serve as catalyst particles for Ge nanowire growth.

The growth process of the Ge nanowires with Bi catalyst particles can be explained by the VLS mechanism.[11] The melting point of Bi (271.3 °C) is much lower than that of Ge (936.3 °C); thus, we expect Bi to evaporate first when the furnace was heated to 1000 °C. Liquidus droplets of Bi condensed on the substrate collector when Bi vapor was brought to lower temperature region (~300 °C) by Ar flow. Ge vapor concentration would increase significantly when the temperature was increased above its melting point (936.3 °C). Continuous adsorption of Ge vapor to the Bi droplet surface resulted in axial nanowire growth after the alloy droplets reach supersaturation. A simple schematic illustration of the in situ Bi particles deposition and Ge nanowire growth processes is shown in Figure
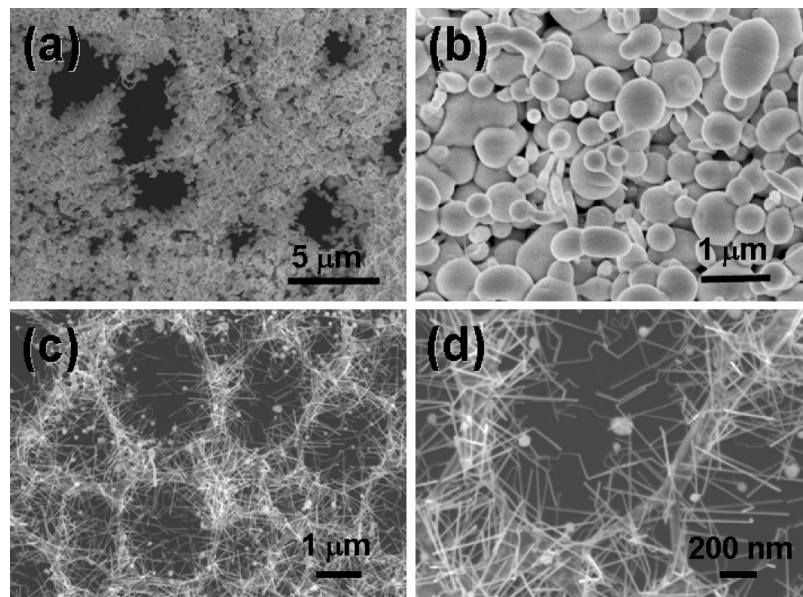
Figure 4. Low and high magnification FESEM images showing the morphologies of products synthesized with Bi/Ge molar ratios of (a and b) 0.2/1 and (c and d) 0.05/1. TEM copper grids coated with holey carbon film were used as substrates to collect the products.
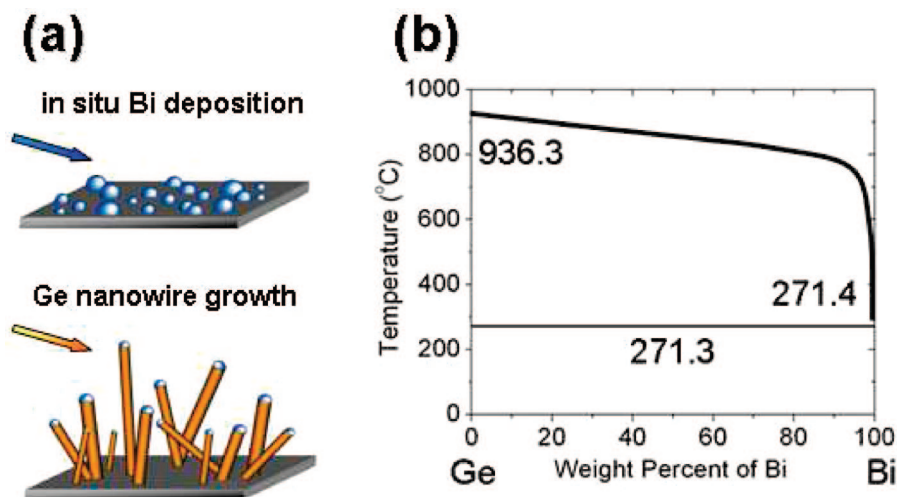

Figure 5. (a) Schematic illustration of the in situ Bi particles deposition and Ge nanowire growth processes; (b) binary phase diagram of Bi−Ge.

5a. This is confirmed by the fact that Bi nanoparticles were found to deposit on the substrate after a short growth run for 1 min (Supporting Information, Figure S1).

Usually the metal catalyst particles or thin films are predeposited on the substrate surface before loading into the furnace for nanowire growth.[12,17,24] In our experiments, the Bi catalyst particles condensed at the low temperature region from the vapor generated via in situ evaporation process. This one-step catalyst deposition and nanowire growth process is expected to minimize the oxidation of the Bi nanoparticles, due to the Ar protection atmosphere in the furnace during growth. Also, the carbon added in source materials plays the role to remove residual oxygen in the furnace chamber and maintain reducing conditions. Prevention of the Bi oxidation is desired for the nanowire synthesis since the thin oxide overlayer on the metal catalyst surface was shown to be highly deleterious for nanowire growth.[25]

For those nanowires synthesized via VLS mechanism, equilibrium binary phase diagram can be used to predict possible catalysts and growth conditions.[26] On the basis of Bi−Ge phase diagram (Figure 5b), Bi is a good candidate for Ge nanowire synthesis since there are no stoichiometric compounds

in Bi−Ge binary systems.[19] Also, the usage of Bi as catalyst for Ge nanowires growth offers two major advantages. First, the solubility of Ge in Bi remains quite low for growth temperatures up to 700 °C (Figure 5b). The low solubility of about 1% (growth temperature around 300 °C) might be critical for the production of, for example, Si−Ge heterostructure nanowires with sharp interfaces.[17,27] Second, the low eutectic temperature of Bi−Ge enables the Ge nanowire synthesis at low temperatures. The eutectic temperature of Bi−Ge (271 °C) is even lower than that of Au−Ge (361 °C).[28] This enables nanowire synthesis under mild conditions, making them compatible with semiconductor integration technologies. Also, low temperature synthesis is desirable for nanowire growth on organic substrates and for solution-phase synthesis to alleviate solvent decomposition.[23,24]

Conclusions

In conclusion, high quality Ge nanowires were synthesized using Bi as catalysts via in situ evaporation method. The growth processes of the nanowires are explained using VLS mechanism.

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Diameters of the nanowires are in the range of 10−40 nm. The as-synthesized nanowires are single crystalline with growth direction along <111>. EDS spectrum and line scanning profile suggest that the nanowires are composed of Ge while the capping catalysts are Bi particles, which confirms the successful vapor-phase synthesis of Ge nanowires using Bi as catalysts. Controlled experiments show that Bi/Ge molar ratio in the source material is a key aspect for the successful synthesis of high quality Ge nanowires.

Supporting Information Available: SEM image of the nanoparticles deposited after a short growth run. This material is available free of charge via the Internet at http://pubs.acs.org.

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