

Germanium Nanowire Growth via Simple Vapor Transport

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Nanoscale one-dimensional (1D) structures have stimulated great interest recently because of their unique electronic, optical, and mechanical properties as a result of their low-dimensionality and the quantum confinement effect.¹ Considerable amount of studies have been documented on the bulk synthesis of nanowires using arc discharge,² laser ablation,^{3–7} template,^{8–11} solution,^{12–15} and other methods.^{16–20} While there are a number of reports on the Si nanowire growth using laser ablation and other approaches,^{1,3,6,21} the growth of Ge nanowire has been sparsely documented.^{3,22} It should be noticed that the excitonic Bohr radius of bulk Ge is much larger (24.3 nm) than that of Si (4.9 nm).²³ Therefore, the quantum size effects will be more prominent in Ge nanowires. Herein we report a simple process to synthesize single crystalline Ge nanowires with diameters less than 30 nm. The nanowires were grown

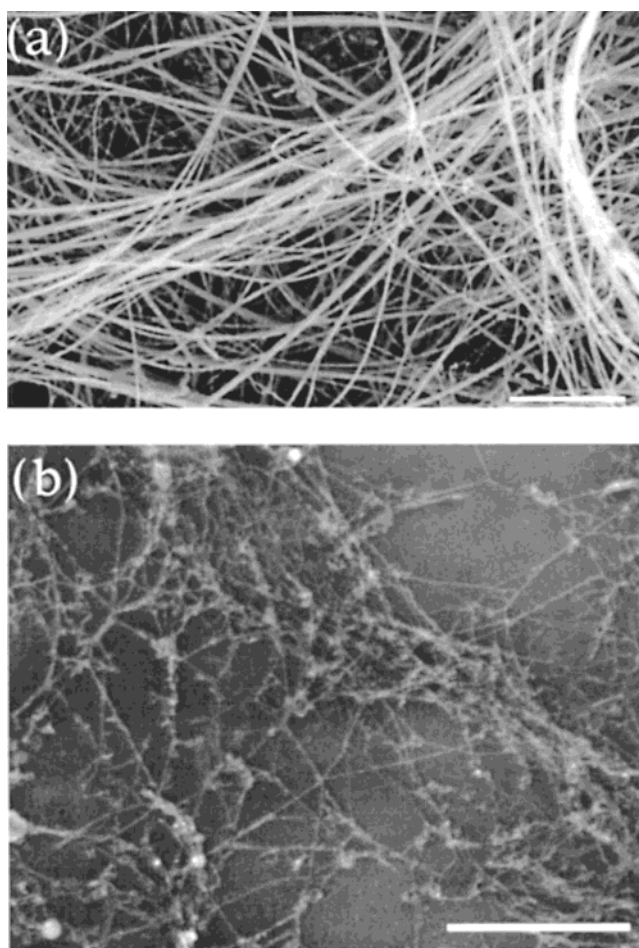


Figure 1. (a) SEM image on as-made germanium nanowires. The scale bar corresponds to 4 μm . (b) SEM image recorded on germanium wires after vacuum thermal treatment. The scale bar corresponds to 1 μm . The images were taken on either JEOL 6400 or JEOL JSM6430 field emission SEM operated at 5 keV.

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using a vapor transport process mediated by vapor–liquid–solid crystal growth mechanism.²⁴

Ge nanowires were grown via a sealed-tube vapor transport process. Briefly, a 30-mg Ge and 7-mg GeI₄ mixture was put in one end of a quartz tube (diameter 0.5 in., length 3 in.), and a gold coated (001) Si substrate was put in the opposite end of the tube. The substrate was coated with 50–200 Å thick gold thin films using Desktop II Denton sputtering system. The tube was flushed with N₂ and evacuated to 30 mTorr. It was then sealed and heated to 1000–1100 °C. The temperature gradient between the source material and the substrate was controlled to be 100–200 °C. After 30 min of the transport reaction, the furnace was air cooled to room temperature. Fluffy brownish products were collected on the Si substrate surface.

Figure 1a shows a typical scanning electron microscope (SEM) image of the as-made nanowires. It was found that the substrate surface was covered with pure nanowires with diameters ranging from 5 to 300 nm.

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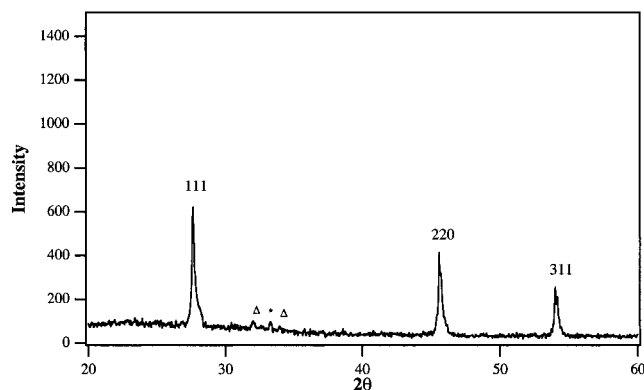


Figure 2. X-ray diffraction pattern recorded on the germanium nanowires. The XRD was obtained on a Siemens D5000 powder diffractometer. Small amount of crystalline I_2 (*) and Au/Ge alloy (Δ) were also detected in the as-made nanowire products.

These wires generally are several hundreds micrometers long. The average size of these nanowires can be controlled by the thickness of the gold thin film deposited on the substrate. Generally thinner coating gives nanowires with smaller diameters, for example, 100 Å Au coating yields wires with an average diameter of 150 nm while wires with average diameters of 80 nm were obtained on substrates coated with 50 Å Au. However, we see no further size reduction when we use a gold coating of less than 50 Å.

In the process of obtaining even smaller and more uniform nanowires, we discovered a simple approach to further reduce the sizes of as-made ones. The obtained nanowires were subjected to a brief vacuum thermal

treatment. The as-made wires were sealed in an evacuated quartz tube and heated for 0.5–1 h at 800 °C in a temperature gradient of 100 °C. After the treatment, we found weblike nanowires covering the entire substrate (Figure 1b) while their average sizes were significantly reduced to 16 nm.²⁵

The purity and crystallinity of these nanowires were examined using X-ray powder diffraction (XRD). Figure 2 shows the diffraction pattern collected on the as-made nanowires. Three diffraction peaks can be readily indexed as (111), (220), and (311) of the crystalline diamond structure of germanium. A small amount of I_2 and Au/Ge alloy was also detected in the product.

Transmission electron microscope (TEM) studies show that the nanowires are straight with uniform diameters, and typically terminated with a nanoparticle at one end. Figure 3a shows a typical image of one such single crystalline nanowire. The nanoparticles at the tip of the wires (Figure 3a, upper inset) generally appear dark and have high contrast compared with the nanowire. Energy-dispersive X-ray analysis (EDX) composition analysis indicates these nanoparticles are made of Au/Ge alloy. The selected area electron diffraction (Figure 3a, bottom inset) recorded on the nanowire exhibits a diffraction pattern consistent with the $\langle 211 \rangle$ zone axis of single-crystal structure of germanium. Indexing the pattern further indicates that the wires are grown predominantly along [111] direction. This is also confirmed by high-resolution TEM image (Figure 3b) that clearly shows the atomic lattice with (111) lattice planes perpendicular to the wire axis.

On the basis of the XRD, TEM, and SEM studies on these wires, we believe these nanowires were grown

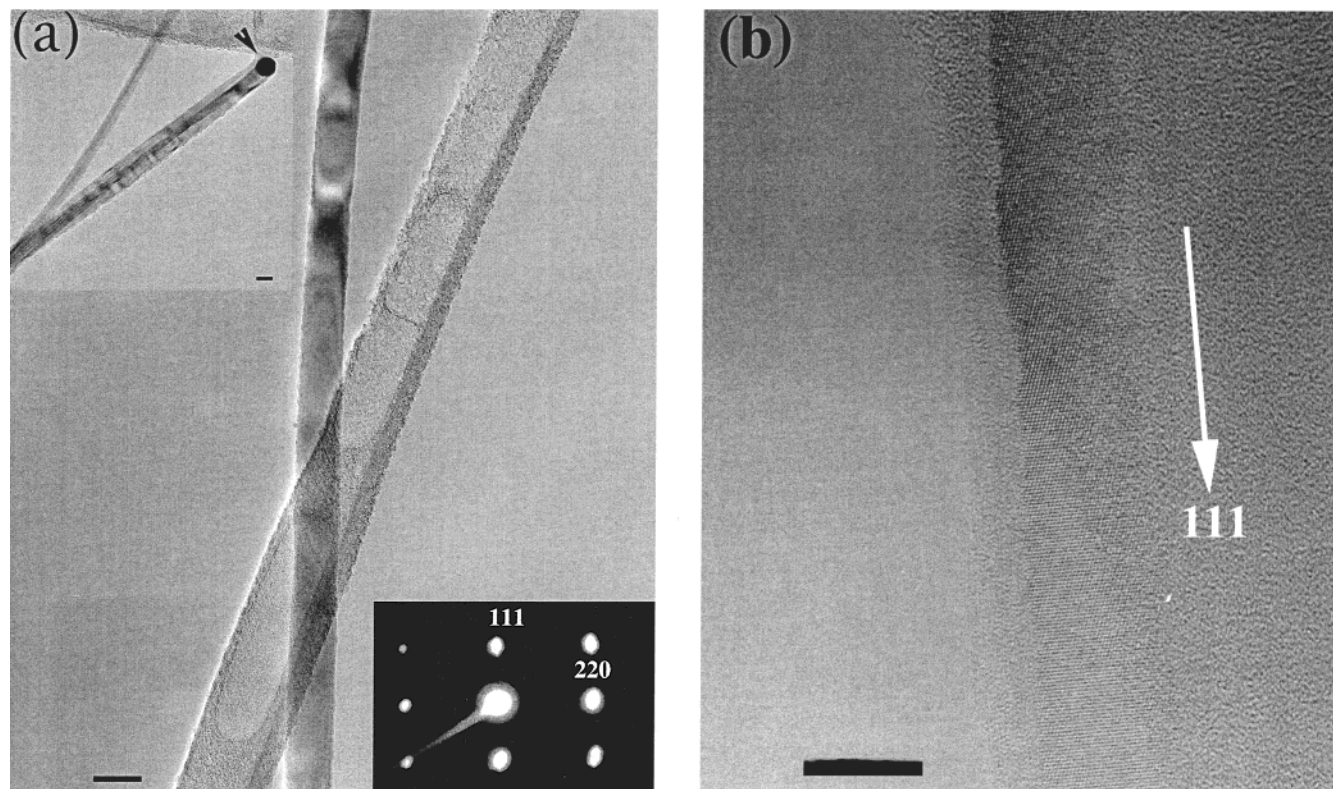
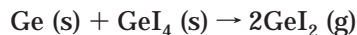


Figure 3. (a) A typical TEM image of germanium nanowire with diameter of 18 nm. The scale bar corresponds to 20 nm. Top inset shows an Au/Ge alloy cluster at the tip of a wire. The scale bar corresponds to 10 nm. Bottom inset shows the SAED pattern recorded along $\langle 211 \rangle$ zone axis. (b) High-resolution TEM image on a 11-nm Ge nanowire. The scale bar corresponds to 10 nm. The images were recorded on a Topcon 002B TEM operated at 200 keV and an Atomic Resolution Microscope operated at 800 keV.

through the well-known vapor–liquid–solid process²⁴ with Au clusters as the catalysts.²⁶ This is apparent from the observation of Au/Ge alloy at the tip of the nanowires. During the transport, the following reaction occurs at high-temperature zone:



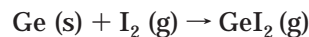
The GeI₂ vapor is then transported to the cold end of the quartz tube, condenses into the gold islands on the heated substrate, and disproportionates according to



The nanosized gold islands serve as the catalysts for one-dimensional germanium crystal growth. Partial decomposition of GeI₄ may contribute to the residue I₂ found in the as-made nanowire products.²⁷

Furthermore, it is interesting that the sizes of these wires can be thermally reduced by a simple evaporation process. This may be due to two possible evaporation/transport processes: (1) direct Ge transport from high-

temperature zone to low-temperature zone, or (2) Ge transport by the residue I₂ in the as-made nanowire products according to²⁸



For wires with such high aspect ratio and high surface area, the surface atom evaporation can be considered to be approximately isotropic and homogeneous in contrast to their anisotropic growth process. Consequently, their size can be significantly reduced.

In conclusion, a simple vapor transport has been employed to synthesize single crystalline germanium nanowires with high yield and high purity. Using a vacuum thermal evaporation process, the average diameter of these wires can be significantly reduced to 16 nm. The synthesis of these single crystalline semiconductor nanowires is expected to open up new possibilities for using these materials as building blocks to create functional two-dimensional or three-dimensional nanostructured materials.

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(25) Interestingly, by using different heat treatment conditions, we can produce wire–tube–wire junctions in high yield (Y. Wu, P. Yang, unpublished results).

(26) Earlier work using GeI₂ as source produced only large Ge single crystalline needles (Wagner R. S.; et al. *J. Met.* **1964**, *16*, 761).

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