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Low-Temperature Synthesis of Single-Crystal Germanium Nanowires by Chemical Vapor Deposition**

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Chemically derived nanowire materials have attracted much attention because of their interesting geometries, properties, and potential applications.^[1–3] Various methods have been developed for synthesizing semiconducting nanowires including laser ablation,^[2,3] physical vapor deposition under high temperatures,^[3–7] and solvothermal growth under high pressures and moderate temperatures.^[3,8–10] Chemical vapor deposition (CVD) has been extensively used for carbon nanotube growth,^[11–13] but is much less explored for the synthesis of semiconductor nanowires, with the exception for silicon.^[14,15]

Herein, we present the first synthesis of single-crystal germanium nanowires, prepared by the CVD of germane (GeH_4) at 275 °C with Au nanocrystals as seed particles. Germanium is an important semiconducting electronic material with high carrier mobility and a band gap of approximately 0.6 eV. Nanowires of germanium were first reported by the group of Heath about ten years ago, synthesized by using a solvothermal approach.^[8] Recently, laser ablation (820 °C),^[2] vapor transport (900–1100 °C),^[4,7,16] and solvothermal methods (300–400 °C, 100 atm)^[9] were used for growth. We show here that high-quality Ge nanowires are synthesized by a simple CVD process at 275 °C under atmospheric pressure. This represents the mildest growth conditions for single-crystal nanowire synthesis. An efficient Ge feedstock

from GeH_4 and the low eutectic temperature of Ge–Au nanoclusters are the key factors that afford vapor-liquid-solid (VLS) growth of Ge nanowires at low temperatures. Further, we show that the CVD approach allows for patterned growth of Ge nanowires, which yields nanowires from well-defined patterned sites on surfaces.

We carried out CVD growth at 275 °C under a 10 sccm (standard cubic centimeter) flow of GeH_4 (10% in He) in tandem with a 100 sccm flow of H_2 in a 2.5 cm furnace reactor (total gas pressure 1 atm) for 15 min. The SiO_2 substrate used in this work contained preformed Au nanocrystals (approximately 20 nm in diameter) deposited uniformly on the surface from a colloidal solution. The inset of Figure 1a shows an atomic force microscopy (AFM) image of the Au particles on a substrate, recorded before CVD. After the

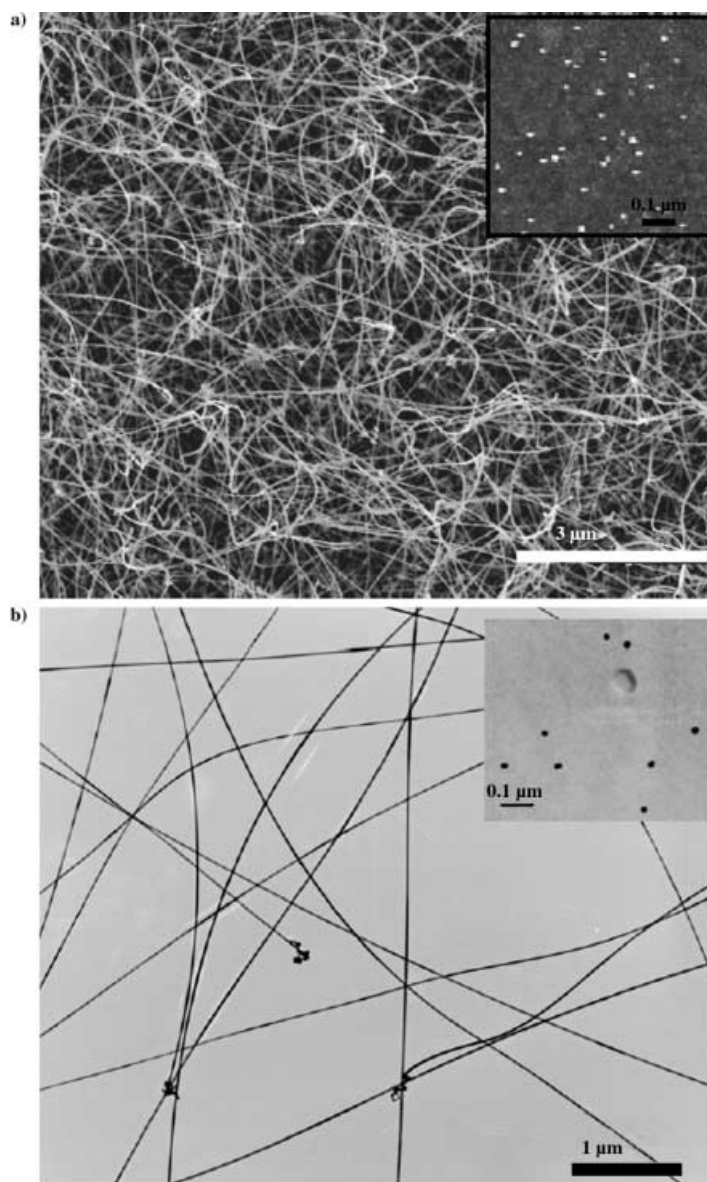


Figure 1. a) An SEM image of Ge nanowires synthesized by CVD at 275 °C on a SiO_2/Si substrate. The inset shows an AFM image of Au nanoclusters on the substrate recorded prior to CVD; b) A TEM image of Ge nanowires synthesized by CVD on a SiO_2 film (approximately 10 nm thick; light background) supported on a TEM grid. The inset shows a TEM image of Au clusters (black dots) on SiO_2 recorded prior to CVD.

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CVD process, characterization by scanning electron microscopy (SEM) revealed high-yield growth of nanowire materials on the substrate (Figure 1a). The nanowires were up to tens of microns in length, and exhibited high abundance and purity without any appreciable amount of particulate by-products.

Transmission electron microscopy (TEM) was used to characterize the high-order structures of our CVD-grown nanowires. In order to investigate nanowires in their as-grown form, we carried out nanowire synthesis directly on TEM grids containing thin (approximately 10 nm) SiO₂ films^[17,18] that are transparent to electron beams. Au nanoparticles were first deposited onto a SiO₂ film (Figure 1b inset), followed by CVD synthesis and TEM imaging without any further processing of the sample (for example, the sonication of nanowires off of substrates in a solution). Figure 1b shows a typical low-magnification TEM image in which nanowires with lengths greater than 10 μm are clearly observed on the SiO₂ film. The clean SiO₂ background and absence of large particulates suggest that our CVD growth conditions produce pure nanowire materials with few impurities.

High-resolution TEM reveals high-quality single-crystalline Ge nanowires grown by CVD. Figure 2a is a high-magnification image that shows the crystal structure of a Ge nanowire. The convergent electron-beam diffraction pattern (Figure 2a, inset) for the nanowire is identified to be along the [011] diffraction zone-axis. The lattice fringes parallel to the viewing direction in the TEM image correspond to the {111} planes (at 54° to the wire axis) of Ge. The spacing between adjacent planes is 3.27 Å, which yields a lattice constant of $a = \sqrt{3}(3.27) \text{ \AA} = 5.66 \text{ \AA}$, a figure which is in excellent agreement with the known diamond crystal structure of Ge. The same lattice constant is derived from the diffraction pattern by using the Bragg formula. The wire axis is identified to be [011̄] based on the [011] zone-axis and analysis of the lattice structure (Figure 2a). The Ge nanowires are single-crystalline over most of their lengths (greater than 10 μm). When following a wire in the TEM, we sometimes observe imaging contrast variations along its length (Figure 1b). This is attributed to slight rotations of the crystal planes resulting from the van der Waals fixation forces of the substrate (that is, slight mechanical twisting of the wire). Careful examinations reveal that many of the as-grown wires do not show such variation along the wire axis for more than 5 μm. Thus far, for approximately 10 wires investigated by high-resolution TEM, all of them have exhibited a [011̄] growth direction (see Figure 2b for a second example). We tentatively conclude that the majority of our Ge nanowires grown by CVD have growth axes along the <110> crystal

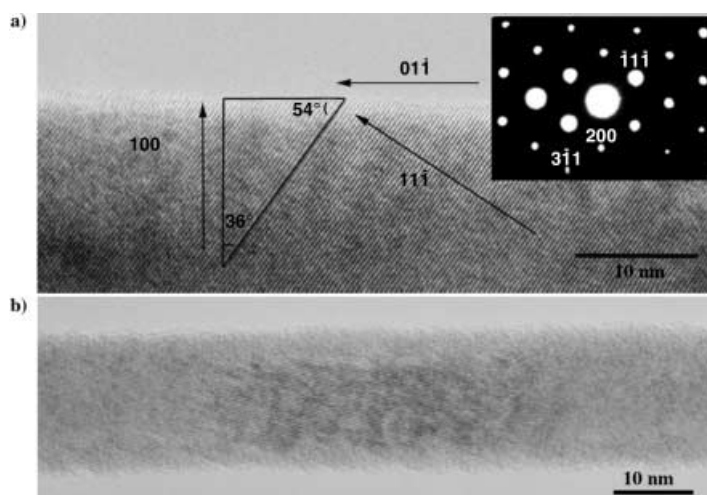


Figure 2. a) A high-resolution TEM image of a Ge nanowire. The inset shows a convergent-beam diffraction pattern; b) TEM image of another Ge nanowire.

direction. In terms of the size of the nanowires, statistical analysis over 40 wires reveals an average diameter of 23 nm, close to the average diameter of the Au colloidal particles.

The synthesis of nanowires directly onto TEM grids allows an examination of the ends of the nanowires in their as-grown states. Figures 3a and b display TEM images recorded for the two ends of a typical nanowire. We observe that one end of the nanowire is tipped with a Au nanoparticle (Figure 3b) and the other end is connected to the SiO₂ substrate (Figure 3a). This result suggests that the growth of Ge nanowires in our CVD process is through the Au particle-seeded VLS mechanism,^[19] similar to that which is observed for Ge wires synthesized by laser ablation^[2] and vapor transport^[3,4,16] methods. The general VLS mechanism involves Ge vapor dissolving into a Au cluster to form an alloy at the initial stage, then under

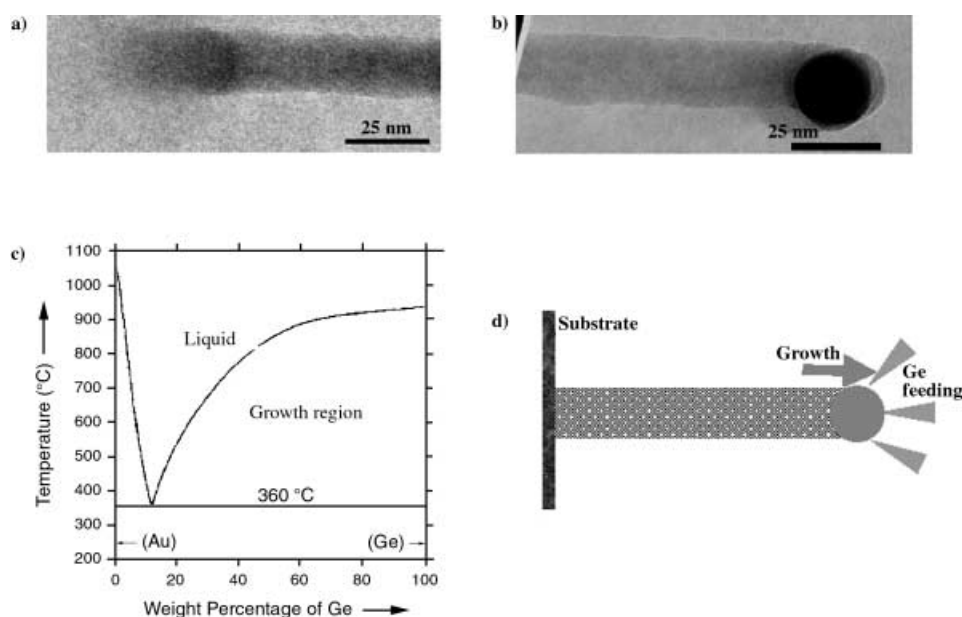
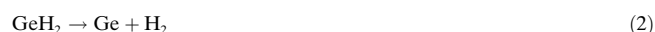


Figure 3. a) A TEM image showing the end of a Ge nanowire connected to a SiO₂ substrate; b) A TEM image of the other end of the same wire shown in (a); c) The binary phase diagram for Ge–Au, adapted from Ref. [20]; d) A schematic drawing depicting the VLS growth process.

continuous Ge feeding the alloy evolves into a liquid state, at which point a further increase in the Ge concentration leads to supersaturation, precipitation, and axial growth of a nanowire.^[2-4,16] The Au cluster is lifted off from its original position on the substrate and extends as the wire lengthens, while the other end of the wire remains connected to the substrate (Figure 3d). This growth process has been clearly observed by Yang et al. using TEM to illustrate an in situ growth experiment where solid Ge is vaporized to feed Au nanoparticles.^[3,16]

There are several important factors that allow for the synthesis of Ge nanowires by our low-temperature CVD process, utilizing the VLS mechanism. The first is related to the conventional Au–Ge binary phase diagram^[20] (Figure 3c). The phase diagram suggests that over a wide range of temperatures above 360 °C (the eutectic temperature), a VLS-type process can take place if the concentration of Ge is increased within the Au particle. When varying the growth temperatures, we find that Ge nanowires can indeed be synthesized up to 600 °C; wires can not be grown below approximately 250 °C. Since the lower limit of our growth temperature (approximately 275 °C) is lower than the eutectic temperature by about 80 °C, we suggest that the melting temperature of the Ge–Au alloy is significantly suppressed for Au nanoparticles from macroscopic Au, for which the conventional phase diagram is derived. This is not surprising considering the well-known phenomenon that nanoclusters often exhibit lower melting temperatures than bulk materials.^[21] The 80 °C reduction in melting temperature for the Ge–Au cluster is an important factor for the growth of Ge nanowires below 300 °C. Nevertheless, further experimental and theoretical work is required to establish phase diagrams for materials with nanoscale dimensions. This shall significantly facilitate the synthesis of a wide range of quasi-one-dimensional materials.

According to the Au–Ge phase diagram, the growth of Ge nanowires, seeded by Au nanoclusters, could occur at low temperatures by the VLS process. An important factor to enable such growth, however, is a suitable Ge feedstock that can provide sufficient Ge species at these temperatures. Laser ablation and physical vapor deposition techniques vaporize solid Ge to feed Au clusters, and the temperatures required to produce sufficient Ge vapor are high.^[2,4,16] Solvothermal methods afford Ge by decomposing precursors in solvents at approximately 300 °C, but at rather high pressures (approximately 100 atm).^[8-9] The choice of GeH₄ as the Ge feedstock in our CVD system is a natural one, but desired nanowire growth results are only obtainable by controlling the GeH₄ decomposition through H₂ addition. Germane can undergo thermal decomposition by the following routes:^[22]



The activation energies for these processes are approximately 50, and less than 35 kcal mol⁻¹ for (1) and (2), respectively. When varying the flow of H₂ during CVD under a constant GeH₄ flow (10 sccm, 10% in He) at 275 °C, we

observed excessive GeH₄ pyrolysis with a H₂ flow rate below approximately 50 sccm, signaled by significant amorphous coatings on the substrate and reactor wall. In strong contrast, for H₂ flow rates greater than 200 sccm, the substrate and CVD were clean and free of appreciable amorphous deposits. However, the growth of Ge nanowires was not observed. This suggests that the increase of H₂ concentration suppresses GeH₄ decomposition (as H₂ is a product in reactions (1) and (2)), leading to an insufficient Ge feedstock for nanowire growth. Active nanowire growth is achieved with a H₂ flow of approximately 100 sccm. Under these conditions, the GeH₄ decomposition is well balanced to provide a sufficient Ge feedstock and avoid excessive pyrolytic Ge deposition. We note that similar H₂ balancing effects have been reported previously in the CVD synthesis of carbon nanotubes from the decomposition of CH₄.^[23]

The synthesis of Ge nanowires by our low-temperature CVD approach, with both high purity and quality, may find many interesting applications. As an example, Figure 4 shows the patterned growth of Ge nanowires. Previously, the patterned growth of carbon nanotubes and other types of wires has been achieved,^[11-13,24] but this is not the case for germanium. We patterned Au nanoparticles in arrays of microsized squares on SiO₂/Si substrates (see Experimental Section) and carried out CVD growth. SEM revealed that Ge nanowires were readily grown from the squares (Figure 4d). The remaining substrate remained clean with negligible particulate deposits. Nanowires emanating from well-defined locations on substrates will facilitate their integration for electrical characterizations and devices. A second direction that we are currently pursuing is to exploit the conditions of soft synthesis. The 275 °C synthesis temperature will allow for the growth of high-quality nanowires on a variety of substrates, including organic materials. Thus far, we have grown Ge nanowires on glass substrates with ease.

In conclusion, we have developed a simple chemical vapor deposition method to synthesize high-purity single-crystalline Ge nanowires at low temperatures. The growth conditions are the mildest for single-crystal nanowire synthesis, and are possible owing to the efficient GeH₄ feedstock and low eutectic temperature for Ge and Au nanocluster seeds.

Experimental Section

Substrate preparation and CVD growth: A Si substrate with a thermally grown oxide layer (500 nm thickness) was cleaned with acetone, methanol, and isopropanol. It was then dipped into a solution of 3-aminopropyltriethoxysilane (APTES, 12 μL in 20 mL H₂O) for 30 minutes, rinsed with deionized water and blow-dried. The substrate was soaked in an aqueous Au colloid solution (20 nm diameter, Alfa Aesar) for 1 h. The APTES monolayer renders the SiO₂ surface positively charged and allows for the deposition of Au colloids (negatively charged) with high efficiency. AFM was carried out with a Digital Instrument Nanoscope III operated in the tapping mode. For CVD, the substrate was placed at the center of a 2.5 cm quartz-tube reactor within a furnace. The reactor was heated to 275 °C under a H₂ flow of 110 sccm. The gas flow was then switched to 10 sccm of GeH₄ (10% in He, Voltaix, NJ) and 100 sccm of H₂ (99.99%, Praxair, CA) for 15 min before switching the gas back to H₂ only, and cooling the system to room temperature.

Electron microscopy: After CVD growth, the substrate was characterized by a field-emission SEM (Hitachi S-800) operated at an accelerating voltage of 25 kV. For TEM, we carried out the growth of Ge nanowires

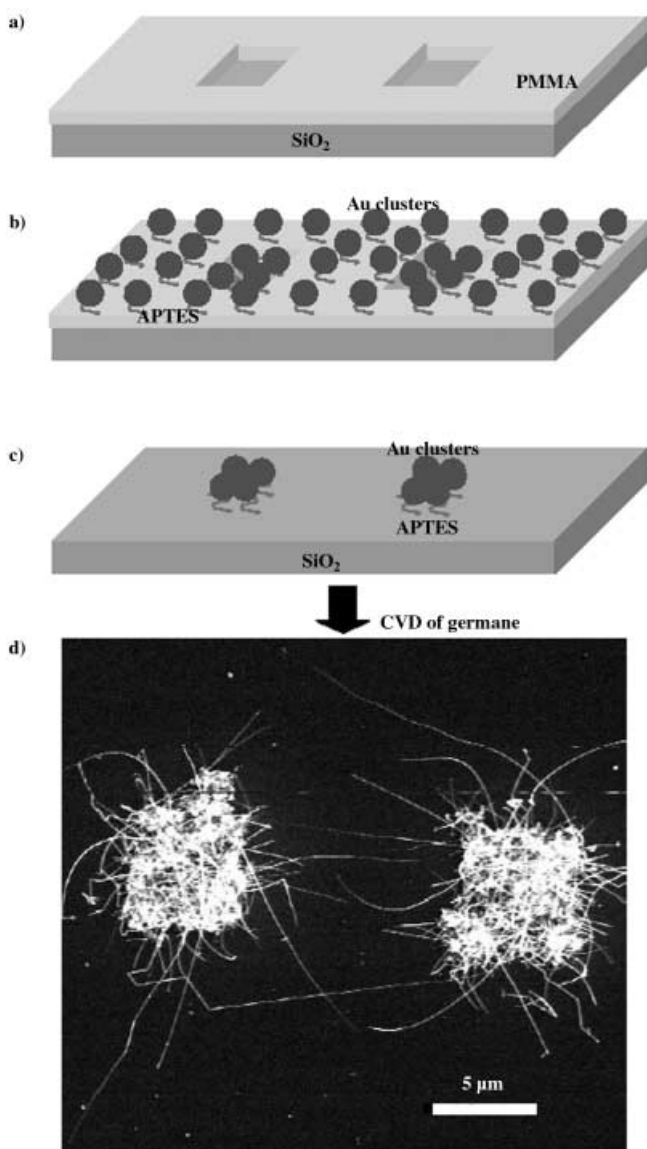


Figure 4. Patterned growth of Ge nanowires on SiO₂/Si. (a)–(c) A schematic describing the process of patterning Au particles into squared regions (see experimental section); (d) An SEM image showing Ge nanowires grown from two square islands containing Au particles.

directly onto TEM grids. Ni grids supporting SiO₂ films (approximately 10 nm thick, Ted Pella) were treated by APTES in the same manner as the SiO₂/Si substrates, followed by Au particle deposition. The grids were imaged by TEM (Philips CM20, operating voltage 200 keV) before the CVD process to characterize the Au particles, and after the CVD process to characterize the grown nanowires and the particle–wire relationship.

Patterned growth: Polymethylmethacrylate (PMMA) was first patterned by electron beam lithography (or photolithography) on a SiO₂/Si substrate to form 5 × 5 μm wells (Figure 4a).^[1] The substrate was treated with APTES and soaked in a Au colloid solution so that Au particles were deposited into the wells (Figure 4b). Removal of the PMMA in acetone affords Au particles that are confined in square islands (Figure 4c). The substrate was then subjected to CVD growth.

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Experimental Observation and Confirmation of Icosahedral W@Au₁₂ and Mo@Au₁₂ Molecules**

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One of the major goals of cluster science is to discover highly stable clusters which may be used as building blocks for novel nanomaterials, such as the celebrated C₆₀. Recently, Pyykkö and Runeberg predicted theoretically a series of highly symmetric and stable clusters containing 12 Au atoms

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