Nanostructures

Deterministic One-to-One Synthesis of Germanium Nanowires and Individual Gold Nanoseed Patterning for Aligned Nanowire Arrays**

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Germanium nanowires (GeNWs) have attracted much attention in recent years[1–9] owing to the advanced electrical properties of germanium, such as high carrier mobilities,[10] and the facile chemical synthesis of single-crystal GeNWs at relatively low temperatures (well below 400 °C).[5] Various synthetic methods for crystalline GeNWs that use gold nanoparticles as seeds have been reported and include chemical vapor deposition (CVD),[5,8,9,11] physical vapor deposition (PVD),[2,3] and solvothermal reactions.[1,4] Never-

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theless, one-to-one growth (1-1 growth) in which each gold particle seed produces one nanowire[12] and the chemistry needed for such growth is not well-established for GeNWs. To achieve this goal is important for the deterministic synthesis of nanowires with controlled yield, size, growth locations, and orientations.

Here, we demonstrate excellent control over the synthesis of GeNWs by low-temperature CVD. GeNWs have been obtained in 100 % yield relative to the gold nanoparticle seeds, and by understanding and optimizing the growth chemistry, we report 1-1 correspondence of GeNWs with gold seeds and that the optimum growth temperature for GeNWs is dependent on the size of the gold nanoparticle. We have also developed a method of patterning individual gold nanoparticles and growing GeNWs in 100 % yield from the well-defined nanoparticle arrays. Furthermore, we show that the orientation of the GeNWs grown from the patterned sites can be manipulated by a post-growth flow-aligning treatment to afford quasi-parallel arrays of GeNWs with well-defined spacing.

The synthesis of GeNWs reported herein is based on a previous CVD method[5] with the slight modification that a low-pressure CVD (LPCVD) system (Figure 1 a) is used instead of the atmosphere-pressure CVD (APCVD) system used previously. GeNWs were grown at various temperatures in the range of 270–400 °C on substrates decorated with preformed gold nanoparticles (diameter, $d = 5$–50 nm) by using GeH_4 as the precursor for germanium. As shown previously, the growth mechanism is well-described by the vapor–liquid–solid (VLS) model.[5,13,14] A main advantage of synthesis by LPCVD over APCVD is that the concentration of GeH_4 in the CVD system is better controlled by varying the pressure in the system than by diluting GeH_4 with carrier gases. The partial pressure of GeH_4 for optimum growth of GeNWs is between 4–8 Torr, below which the yield of nanowires is low as a result of insufficient feedstock and above which undesirable pyrolysis of GeH_4 is observed. Another important advantage of the LPCVD approach is the rapid removal by vacuum pumping of O_2 and H_2O trapped in the system which efficiently reduces the contaminants in the system and leads to highly reproducible growth results between experiments.

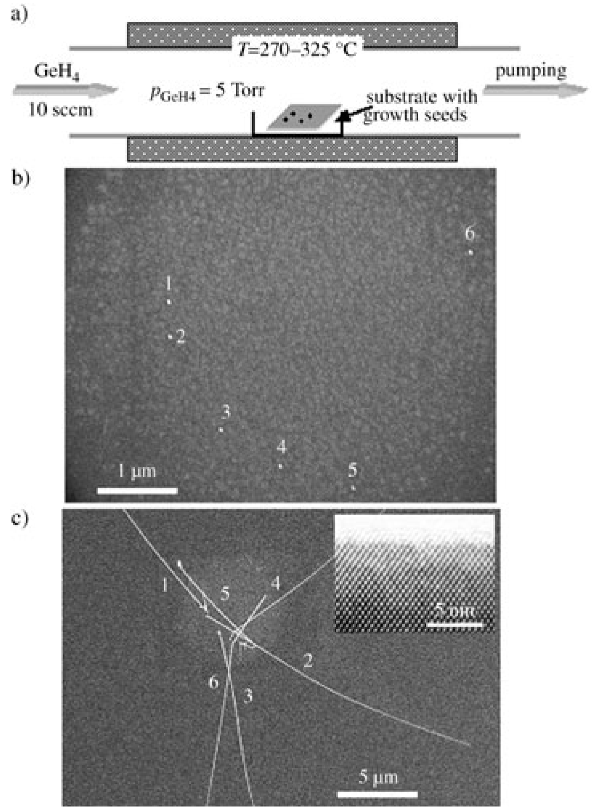

Figure 1. One-to-one growth of 20-nm GeNWs. a) Schematic of the LPCVD setup (sccm = standard cubic centimeters per minute), b) SEM image of six gold nanoparticles ($d \approx 20$ nm) as growth seeds, and c) SEM image of the six GeNWs grown from the gold seeds labeled in (b). (The inset shows a high-resolution transmission electron microscopy image of a single-crystalline GeNW grown under the same conditions as those shown in the main panel).

The main outcome of the current work is that the optimum growth condition of GeNWs is size-dependent; that is, the temperature at which optimum 1-1 growth of GeNWs is observed varies with the size of the gold seeds. Under a fixed partial pressure of GeH_4 (p_{GeH4}) of 5 Torr, the optimum growth temperature for gold seeds of diameter $d = 20 \pm 2$ nm is around 295 °C, under which temperature every gold seed can produce a GeNW (Figure 1 b and c). The total number of nanowires grown matches the number of starting gold nanoparticle seeds, and the nanowires originate from the positions of the starting particles (Figure 1 b). The quantitative yield and 1-1 growth at 295 °C for the 20-nm particles are robust and have been reproduced with ten batches of samples. For larger gold seeds ($d = 50 \pm 3$ nm), the optimum growth temperature for the GeNWs is approximately 310 °C and 1-1 growth was observed (Figure 2 b). At a lower temperature of

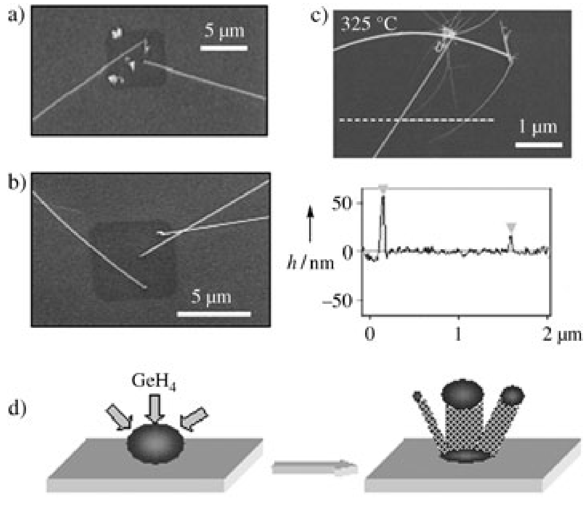

Figure 2. Growth results from 50-nm gold seeds at a) 295, b) 310, and c) 325 °C. Several blotches in (a) correspond to gold particles that have failed to produce nanowires. 1-1 growth is observed in (b) which suggests that the optimum growth of nanowires occurs at 310 °C for 50-nm seeds. The lower panel in (c) is a height (h) profile measured by atomic force microscopy (AFM) of GeNWs grown at 325 °C which shows that smaller ($d \approx 20$ nm) nanowires grow alongside 50-nm GeNWs. d) A schematic of multiple nanowires grown from one large parent particle.

295 °C, not all of the 50-nm gold seeds were capable of producing GeNWs (Figure 2a). On the other hand, if the growth temperature was high (e.g. at 325 °C), the 50-nm gold seeds produced more GeNWs than the number of starting seed particles and, interestingly, nanowires with diameters that are much smaller than the starting particles ($d \approx 50$ nm) were observed (Figure 2c). This observation suggests that splitting of the gold seeds with $d \approx 50$ nm into smaller particles occurred to produce smaller nanowires at the higher growth temperature (Figure 2d).

The optimum growth temperatures of GeNWs by CVD for gold seed particles with diameters in the range of 5 to 50 nm are summarized in Figure 3. A general trend is that smaller gold seeds can nucleate and grow nanowires at lower temperatures. For large particles ($d \approx 50$ nm) a low growth temperature produces GeNWs in low yields, and too high a temperature tends to overproduce wires as a result of splitting of gold seeds. These results can be explained by considering several key factors involved in the VLS growth process. The first factor is that the eutectic melting temperature of Ge–Au is size-dependent and higher for larger particles. Such size-dependence of the melting temperature has been documented for single- and binary-element particles.[15,16] It is therefore reasonable that larger particles require a higher temperature for efficient supersaturation and growth to occur. Second, diffusion of germanium in the gold particle is an important kinetic factor of the VLS growth process. The size of the gold seeds determines the length over which germanium must diffuse to saturate the Ge/Au solution for nucleation and growth of one nanowire from the seed particle. Higher temperatures will facilitate diffusion of germanium and thus the growth of nanowires from larger particles. The third factor is the feedstock supply of germanium. Higher temperatures will lead to more-efficient decomposition of the GeH_4 precursor and provide an efficient supply of germanium needed for larger gold particles.

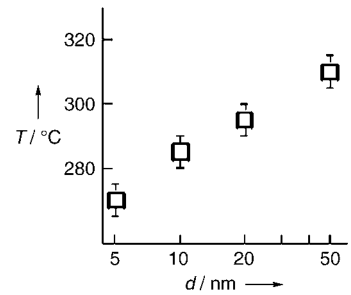

Figure 3. Size-dependent conditions for the growth of nanowires. A plot of the optimum temperature (*T*) for growth of the GeNW as a function of the size of the gold particle seeds, and hence the size of the nanowire, by CVD under a fixed partial pressure of 5 Torr of germane. For each particle size, the optimum growth temperature is denoted by a hollow square and the error bars span less than 10 °C.

The VLS growth of nanowires from large gold seed particles appears to be diffusion-limited. At high temperatures, the feeding of germanium precursor could be rapid while the diffusion of the feedstock atoms in gold may not be sufficiently high to supersaturate a large particle. Rather, smaller regions of the gold cluster are supersaturated rapidly, which leads to nucleation and growth of smaller nanowires from the parent gold particle (Figure 2d). In a control experiment, we attempted to grow germanium and silicon nanowires from GeH_4 and SiH_4, respectively, by using ultra-large gold particles with $d \approx 250$ nm. At all of the temperatures tested, we were unable to observe 1-1 growth from these large particles and always observed the growth of only small wires as a result of splitting of the gold particles. We believe that the diffusion limitation for the growth of large nanowires and the size-dependent growth of nanowires is general to the synthesis of various nanowire materials by the VLS mechanism.

With the 1-1 growth understood, we next pursued patterning of individual gold nanoparticles to achieve 1-1 growth of GeNWs at controlled locations and with mono-dispersed sizes by first using electron-beam lithography to pattern arrays of small gold islands on a substrate (Figure 4a). The islands were 40-nm wide with various thicknesses (1–10 nm) and were formed by an evaporation and lift-off technique. Upon annealing at 300 °C, Au atoms in each island aggregated to form well-defined gold dots with controllable diameters in the range of 5–50 nm (the size of the dot is dependent on the thickness of the metal in the 40-nm-wide islands). Figure 4b shows an array of regularly spaced gold particles with $d \approx 20 \pm 3$ nm formed by this method. CVD growth using the optimum conditions identified in Figure 3 for 20-nm gold seeds led to successful 1-1 growth of GeNWs from the nanoparticle arrays (Figure 5). This result demonstrates that the synthesis of nanowires can be well-controlled at the single-particle level by making use of the understanding of the growth of nanowires as well as the state-of-the-art lithographic patterning technique.

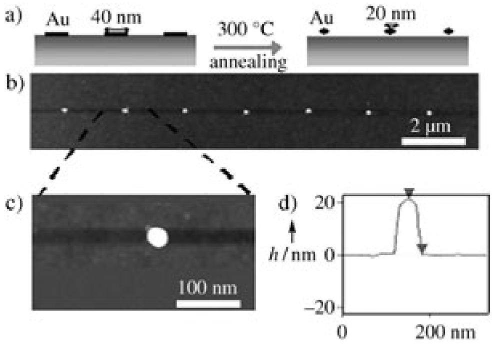

Figure 4. Patterning of individual gold nanoparticles. a) Schematic of the patterning process, b) AFM image of an array of Au dots regularly spaced at 2 µm, c) magnified AFM image of one gold nanoparticle, and d) height profile that shows the size of the gold nanoparticle ($h \approx 20$ nm) in (c).

We also explored the possibility to control the orientations of the GeNWs in an approach that utilized fluid flow[17,18] to manipulate and reorient the GeNWs grown from the patterned gold particle arrays, as shown schematically in Figure 5a. In the VLS tip-growth process, one of the ends of an as-grown GeNW is anchored onto the substrate at the point from which it grows, as highlighted by arrows in

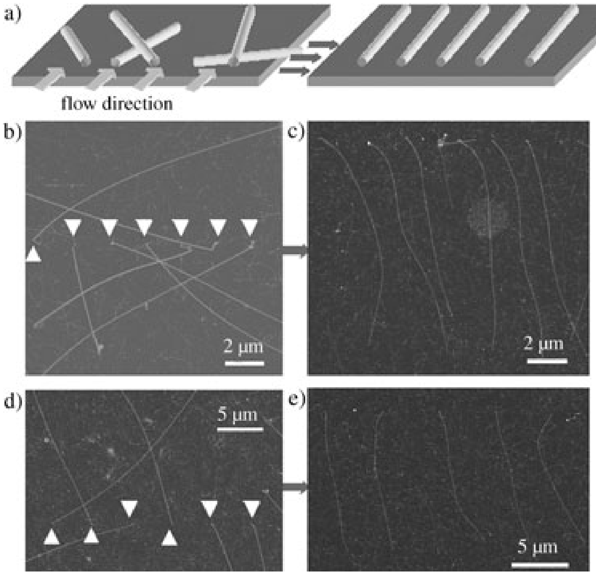

Figure 5. Post-growth reorientation of nanowires. a) Schematic of the process to flow-align GeNWs grown from an array of patterned gold seeds, b) SEM image of GeNWs grown from an array of 20-nm Au dots similar to those in Figure 4b (the arrows indicate the original positions of the Au dots and the fixed ends of the as-grown GeNWs), c) SEM image of quasi-aligned GeNWs (2-μm pitch) after flow treatment of the sample in (b), and d) and e) SEM images of GeNWs grown in a one-to-one manner from patterned Au dots (5-μm pitch) before (d) and after (e) flow-alignment.

Figure 5b and d, and acts as a pivotal point for the wire. After a stream of deionized water is flowed across the substrate surface, the nanowires are reoriented towards the flow direction and become quasi-aligned while maintaining the same spacing between their pivoted ends (Figure 5c and e).

In summary, we have demonstrated controlled one-to-one synthesis of GeNWs in near-quantitative yields from gold seed particles. Size-dependent optimum growth conditions for the GeNW have been identified. For gold seeds with diameters of less than 50 nm, underproduction, 1-1 growth, and overproduction can occur depending on the conditions. Growth of large GeNWs appears to be diffusion-limited. These results have generic implications in the synthesis of other types of nanowires through the VLS mechanism. Patterning and positioning of individual gold nanoparticles was observed by lithographic patterning and used for successful one-to-one nanowire growth. Finally, post-growth flow-alignment was used to obtain quasi-parallel nanowires that originate from well-controlled locations. These results are important to the fundamental synthesis of nanomaterials and may find important applications in various fields including high-performance nanoelectronics.

Experimental Section

Deposition of preformed gold nanoparticles: A silicon substrate was soaked in an aqueous solution of 3-aminopropyltriethylsilane (APTES; 12 μL APTES in 20 mL H_2O) for 2 minutes. After thorough rinsing with deionized H_2O and blow-drying with N_2, the substrate was then soaked in a solution of Au colloids (5–50 nm) for 5 minutes. The resulting density of Au particles on the substrate was determined by the concentration of the colloidal solution. For instance, a prepared solution of 20-nm Au colloids (Ted Pella, Inc., CA, USA) contains 10^{11} nanoparticles mL^{-1}. Dilution by 1000 was performed to obtain a concentration of 10^8 cm^{-3}. When deposited on a silicon substrate, a density of approximately 1 particle/3 μm^2 could be reliably obtained with such a concentration. After deposition of Au nanoparticles, calcination in air at 300°C for 15 minutes was carried out to remove organic residues. The as-prepared substrate was imaged by scanning electron microscopy (SEM, FEI XL30 Sirion) to record the locations of individual nanoparticles in certain regions. Then, the substrate was subjected to CVD growth followed by SEM imaging of the same regions to correlate the synthesized nanowires with their parent nanoparticle seeds.

CVD synthesis of GeNWs: In a typical experiment, the CVD quartz tube chamber (2.54 cm) was first evacuated to its base pressure of 150 mTorr and then heated up to a growth temperature in the range of 270–325°C. The chamber was then filled with precursor species of GeH_4 (germane, 10% in He, Voltaix Inc. NJ, USA) to the desired growth pressure (total pressure $\approx$ 50 Torr, $p_{GeH4} \approx 5$ Torr) and maintained at that pressure throughout the growth. During this process, GeH_4 was flowed at a rate of 10 sccm (standard cubic centimeters per minute). At the end of the reaction, the feeding of GeH_4 was stopped and the chamber was pumped to its base pressure again and cooled down to room temperature. (One of the criteria of optimum growth is that the quartz growth chamber after CVD should be free of pyrolytic deposits of GeH_4).

Patterning of individual gold nanoparticles: A 100-nm-thick film of polymethylmethacrylate (PMMA) was formed by spin-coating onto a Si substrate. Electron beam lithography (Raith 150) was used to create wells in the PMMA film with dimensions of 40×40 nm^2. A Au film of 1–10 nm thickness was then deposited onto the PMMA-patterned substrate in an electron-beam evaporator, followed by lift-off of the PMMA to afford 40-nm-wide Au islands. The substrate was then annealed in Ar at 300°C for 15 minutes during which time the small Au islands aggregated to form single Au nanoparticles.

Manipulating the orientations of nanowires after one-to-one growth**:** After CVD growth of GeNWs on a substrate with patterned Au dots, a droplet of H_2O was placed onto the substrate to cover the as-grown GeNWs. N_2 was then flowed to blow-dry the surface along a desired direction. After this simple process, the nanowires were quasi-aligned with the flow direction.

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