



## Synthesis of Si-Ge Oxide Nanowires via the Transformation of Si-Ge Thin Films with Self-Assembled Au Catalysts

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A technique has been developed to transform a Si-Ge thin film into Si-Ge oxide nanowires with the assistance of Au particles through a three-step annealing process. A honeycomb network of Au colloidal nanoparticles was self-assembled; 400°C annealing removes the surface surfactant; 800°C annealing forms hexagonally self-assembled Au particles on the thin-film surface; finally, a 1075°C annealing results in the growth of oxide nanowires on the surfaces of Au particles. Synthesized nanowires have an emission peak at 3.3 eV. This technique is useful for growing silicon oxide nanowires with a tunable amount of Ge doping.  
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One-dimensional (1D) and quasi-one-dimensional (quasi-1D) nanostructures are attracting a great deal of attention due to their unique properties and novel applications.<sup>1,2</sup> Oxides are the basis of smart and functional materials that have tunable properties and important technological applications.<sup>3-5</sup> Recently, silicon-based nanowires<sup>6-9</sup> are of great interest due to their potential applications in nanoscale optoelectronics,<sup>10,11</sup> sensing and field emission.<sup>12,13</sup> The silicon-based nanowires were mainly synthesized by a vapor-liquid-solid (VLS) process either by thermal evaporation or laser-assisted vaporization techniques, in which the source materials are located inside a tube furnace and the substrate is placed downstream apart from the source materials.

In this article, we report a technique that transforms a thin film of SiGe into Si-Ge oxide nanowires with the assistance of gold catalysts deposited directly onto the thin film. A self-assembled honeycomb network of Au colloidal nanoparticles was first formed without using lithography. After 400°C annealing, the surfactant passivated on the Au colloidal nanoparticles was vaporized, and a subsequent annealing at 800°C forms hexagonally self-assembled Au particles on the thin film surface. Finally, an annealing at 1075°C results in the formation of the nanowires on Au particles. In comparison to silicon oxide light-emitting material,<sup>10,11</sup> Si<sub>1-x</sub>Ge<sub>x</sub>O<sub>2-y</sub> nanowires is a new material that allows optical devices to operate at a slightly higher energy.<sup>14</sup>

The synthesis was made on 700 nm thick Si<sub>0.8</sub>Ge<sub>0.2</sub> and 200 nm thick low-temperature Si buffer layers grown on Si (100) wafers by ultrahigh vacuum chemical vapor deposition (UHV-CVD). The gold catalyst colloidal nanoparticles were synthesized by a two-phase method.<sup>15</sup> In order to achieve a highly ordered pattern of Au nanoparticles on the film, Au colloidal particles passivated with tetraoctylammonium-dodecanethiol (TOAB-DT) with narrow size distribution were used.<sup>16,17</sup> Dispersion solutions of Au nanoparticles were prepared with 0.125, 1, and 5.36 g of gold nanoparticles/liter of toluene (g/L). A 30 μL droplet of each dispersive solution of Au nanoparticles was drop-cast with a micropipet on (5 × 5) mm<sup>2</sup> Si<sub>0.8</sub>Ge<sub>0.2</sub>/Si samples. The solvent was evaporated while placing the substrate in an air-extracting apparatus with appropriate airflow, humidity, and temperature.

Samples were then placed into a horizontal quartz tube furnace. The temperature was kept at 400°C for 30 min in a N<sub>2</sub> ambient. Subsequently, the furnace was heated up to 800°C for 60 min to form the regular hexagonal Au network. After annealing at 1075°C for 10 min, the Si<sub>1-x</sub>Ge<sub>x</sub> oxide nanowires were obtained.

Morphological studies of the grown nanostructures have been performed by transmission electron microscopy (TEM) and scan-

ning electron microscopy (SEM). TEM examination was carried out by using a JEOL 2010 TEM at 200 kV with a point-to-point resolution of 0.23 nm. SEM observation was conducted by using a JEOL JSM-6500 FESEM operating at 15 kV with a point-to-point resolution of 1.5 nm. An energy dispersive spectrometer (EDS) attached to the TEM was utilized to determine the chemical composition. For the EDS analysis, the electron beam can be converged to as small as 1.5 nm in size.

The cathodoluminescence (CL) spectra were obtained in the SEM with an electron probe microanalyzer (Shimadzu EPMA-1500). CL spectra were accumulated in single shot mode within a short time of 1 s and with a spectral resolution of 4 nm. In general, the CL excitation was performed with a beam current of about 100 nA in TV scanning mode over an area of 2.9 × 10<sup>-5</sup> cm<sup>2</sup>.

Dispersion solutions of Au nanoparticles were drop-cast onto a Si<sub>0.8</sub>Ge<sub>0.2</sub>/Si wafer. After the solvent was evaporated, the Au nanoparticles were distributed into regular honeycomb structures by self-assembly (Fig. 1a) similar to the case on Si.<sup>16,17</sup> It was observed unequivocally by in situ optical microscopy that the hexagonal network was formed from the condensation of water droplets, arranged in hexagonal form, from the air moisture. The water droplets condensed on the evaporating dispersion and self-organized into an ordered array that templated the deposition of hydrophobic nanocrystals.<sup>17,18</sup>

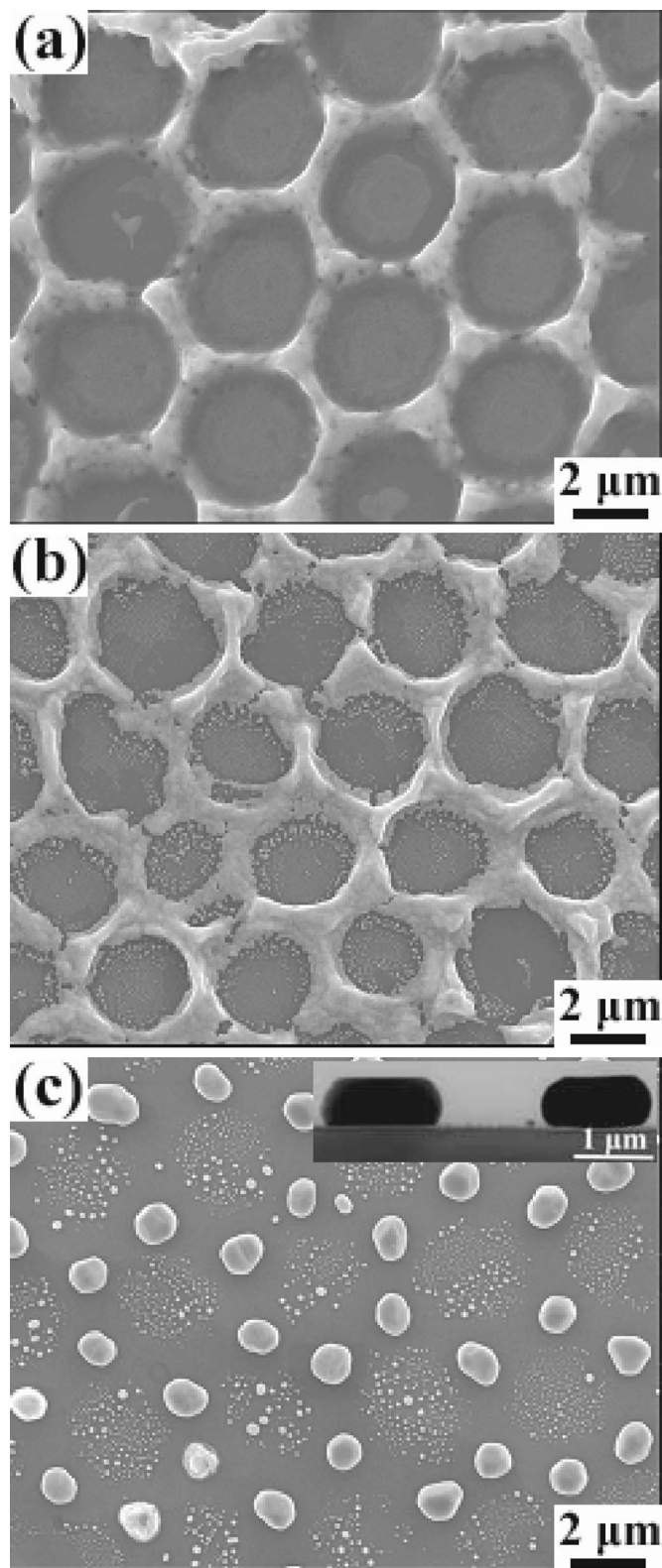
The surface passivation on gold nanoparticles was removed by annealing.<sup>17,19</sup> To form the honeycomb network, a two-step annealing procedure was used. First, the samples were annealed at 400°C for 30 min to vaporize the organic surfactant, while the integrity of the honeycomb network was still maintained. The ribbons of honeycomb network were found to thin down as well as to become disconnected, as shown in Fig. 1b, possibly due to shrinkage in volume. After the second consecutive moderate-temperature annealing at 800°C for 1 h, the ribbons of honeycomb were observed to aggregate to the intersection, forming a hexagonal dot array. The annealing also consolidated the voids and/or bubbles induced by the evaporation of the organic compound at the colloidal surface. The recrystallization process observed in Fig. 1c is likely driven by the minimization of surface energy, during which the cracking induced in the walls of the honeycombs during the moderate-temperature annealing at 800°C defines the hexagonal distribution of the large Au particles after recrystallization. Some smaller Au particles were also formed in the hexagonal mesh. A cross-sectional TEM image of the Au particles on the thin-film surface is shown in the inset of Fig. 1c. The particles were verified as pure gold by EDS analysis. From the Au-Si, Au-Ge, and Au-Ge-Si phase diagrams,<sup>20</sup> no equilibrium Au compounds are expected to form. After cooling down to room temperature, the nonequilibrium eutectic Au-Si-Ge liquid droplets tended to segregate and the pure Au particles were obtained.<sup>21,22</sup>

Further heating of the sample to a higher temperature results in the growth of nanowires. Figure 2a shows a SEM image of the sample that was heated at 1075°C for 1 min, revealing the initial

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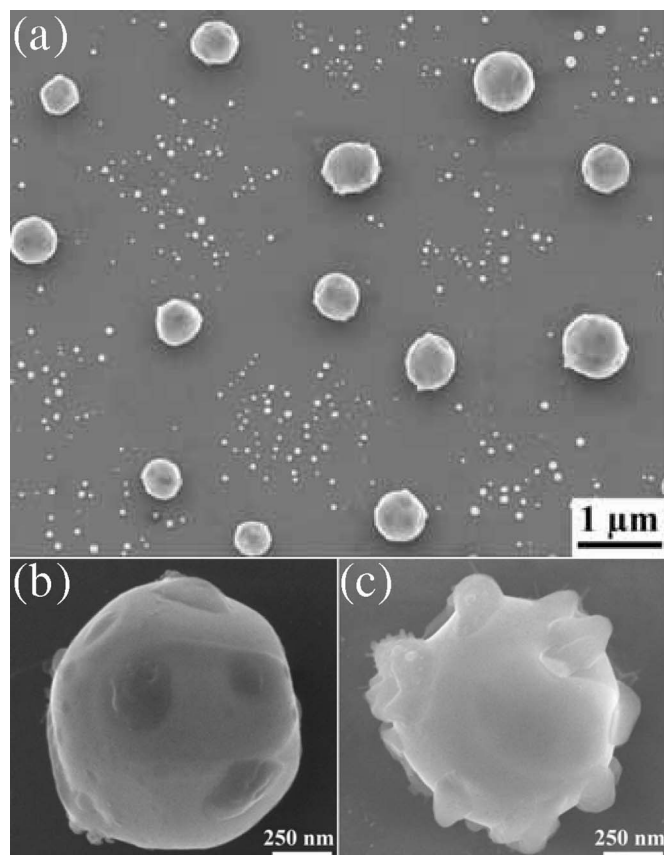
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**Figure 1.** (a) Honeycomb structure formed by drop-cast of Au nanoparticle solution on the  $\text{Si}_{0.8}\text{Ge}_{0.2}$  wafer, (b) after annealing at  $400^\circ\text{C}$  for 30 min, (c) the hexagonal Au particle network formed after annealing at  $800^\circ\text{C}$  for 60 min and its corresponding cross-sectional TEM image (inset).

growth stage of the Si-Ge oxide nanowires on a hexagonal Au particle network. There were several nanowires grown on the Au surface. Higher magnification images of the sample at this stage are



**Figure 2.** (a) Top-view SEM image of an annealed sample at  $1075^\circ\text{C}$  for 1 min, revealing the initial growth of the Si-Ge oxide nanowires, (b) and (c) higher magnification images of the samples at this stage.

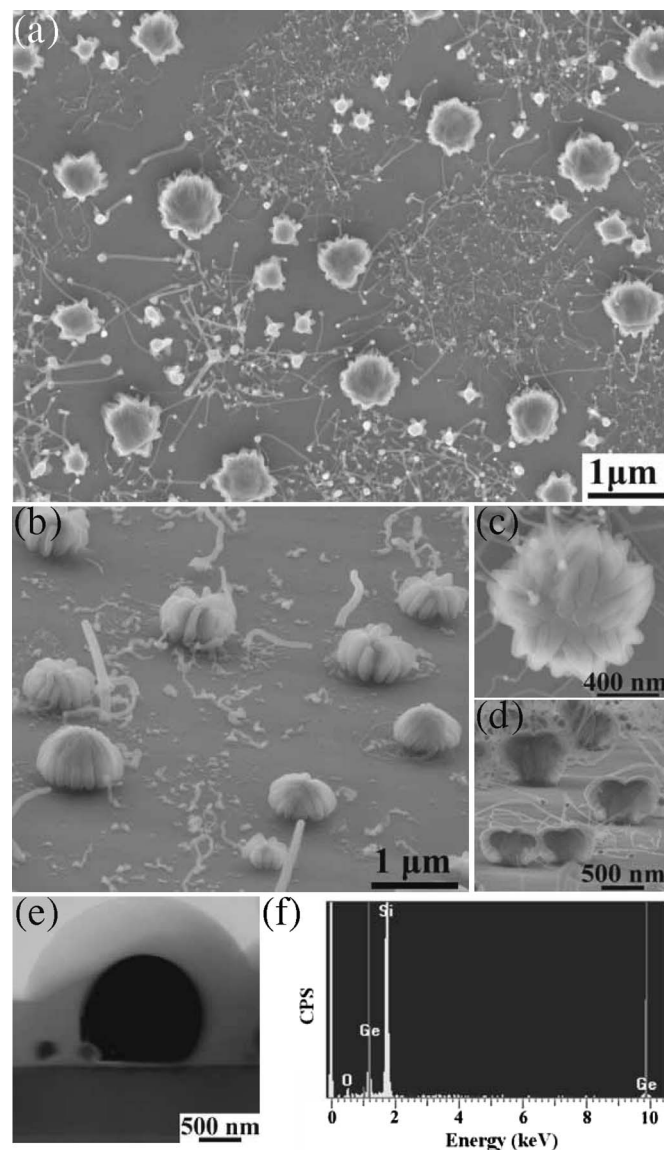
shown in Fig. 2b and c. The distinct characteristic is that several nanowires were grown from a single large Au particle. Since the eutectic droplets are too large to keep uniform distribution of Si and Ge atoms across its surface, simultaneous growth of several nanowires is possible on the surface of the Au catalysts. Similar phenomena have been reported for Ga and Ge droplets.<sup>23</sup>

As the sample was held at  $1075^\circ\text{C}$  for 10 min, the hierarchical fireball-like nanowire network mediated by a self-assembled hexagonal catalyst was obtained. The typical top view and  $20^\circ$ -tilted side view SEM images of hierarchical fireball-like nanowire network are shown in Fig. 3a and b, respectively. The magnified top view image of the fireball-like Si-Ge oxide nanowire structure is shown in Fig. 3c. There are numerous nanowires of uniform diameter grown on the single Au particles, resulting in fireball-like nanostructures. In addition, once the eutectic droplets were well-mixed and supersaturated at high temperature, wire precipitation tended to occur at the solid-liquid interface. An  $80^\circ$ -tilted side view magnified SEM image shows that the growth of nanowire between Au particles and the  $\text{Si}_{0.8}\text{Ge}_{0.2}$  substrate occurred, as seen in Fig. 3d. TEM image and EDS spectrum, as shown in Fig. 3e and f, further indicated that the nanowires are amorphous and their compositions were measured to be Si:Ge:O = 63%:15%:22% on average. The Si:Ge ratio is close to 4, in correspondence to the composition of the thin film of  $\text{Si}_{0.8}\text{Ge}_{0.2}$ . But the content of oxygen could be underestimated due to the fluorescence effect in EDS analysis of light elements.

The growth is governed by the VLS process. The Si-Ge layer vaporized under high temperature, and it redeposited on the surface of the liquid Au droplets. With the presence of residual oxygen in the growth chamber and the possible presence of an oxide layer on the top of the Si-Ge thin film, Si-Ge oxide nanowires were grown.

The CL spectrum of the hierarchical fireball-like Si-Ge oxide

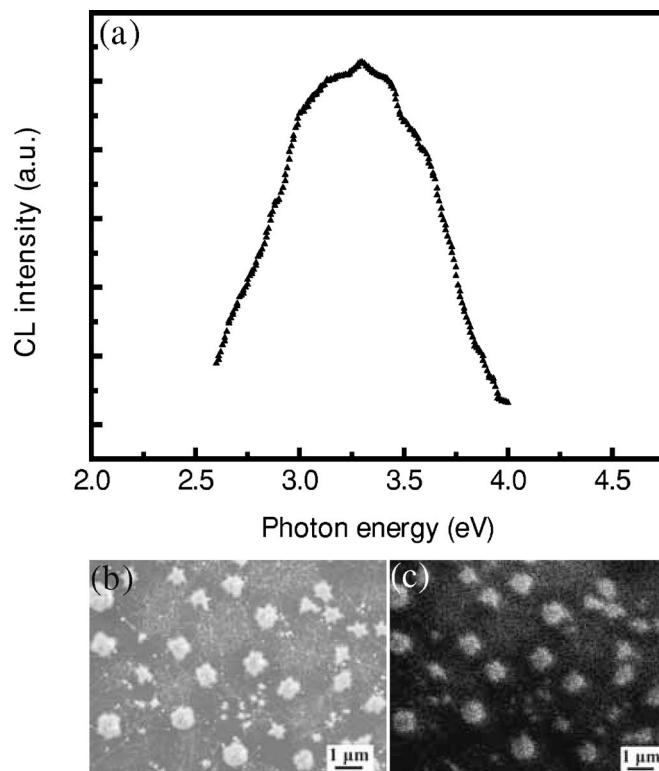




**Figure 3.** (a) Top view and (b) 20°-tilted side view SEM images of the Si-Ge oxide nanowire network with fireball-like structure, (c) higher magnification top view image, (d) 80°-tilted side view image, (e) cross-sectional TEM image, and (f) corresponding EDS spectrum of Si-Ge oxide nanowire structure.

nanowires is shown in Fig. 4a. A peak centered at 3.3 eV (379 nm) was observed. Since the nanowires were chemically nonstoichiometric, obviously the interrelated behavior of the 3.3 eV CL band was ascribed to charge carriers being located either at the Si or Ge sites of mixed  $O_3 \equiv Si-Ge \equiv O_3$  and  $O_3 \equiv Ge-Ge \equiv O_3$  vacancies, which would result in a higher emitted energy of Si-Ge oxide nanowires than that of Si oxide nanowires.<sup>14</sup> Figure 4b is the SEM image of fireball-like  $Si_xGe_{1-x}$  oxide nanowire network, from where the CL signals were acquired. The corresponding luminescence mapping by selecting the CL peak from the region is shown in Fig. 4c. Bright dots in the image revealed the luminescence sites, which coincide with the positions of the hexagonal structure Si-Ge oxide nanowire network. Some other bright dots derived from the interior coincide with the thin Si-Ge oxide nanowires catalyzed by the smaller Au nanoparticles on the substrate.

In summary, we report a technique that transforms a thin film of Si-Ge into Si-Ge oxide nanowires (silicon oxide nanowires doped with tunable amount of Ge) with the assistance of gold catalysts



**Figure 4.** (a) The CL spectrum of the Si-Ge oxide nanowire structure, (b) SEM image showing the Si-Ge oxide nanowires, and (c) corresponding CL mapping.

deposited directly onto the thin film. The morphology, structure, and optical property have been studied by scanning electron microscopy, cathodoluminescence measurement, and transmission electron microscopy. Fireball-like Si-Ge oxide nanowire network could be formed by annealing samples at 1075°C for 10 min in  $N_2$  ambient. TEM and EDS analysis show that the nanowires are amorphous and have an average chemical composition of Si:Ge:O = 63%:15%:22%. Owing to the doping Ge atoms in oxygen-deficient nanowires, room temperature CL spectra of the synthesized Si-Ge oxide nanowires showed a strong deep blue emission peak at 3.3 eV (379 nm). According to the CL mapping image, it could be found that the main light-emitting sites coincide with the positions of the Si-Ge oxide nanowire network. This technique has the potential for growing Ge-doped silicon oxide nanowires on large-size silicon-based substrates.

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