RAPID COMMUNICATIONS

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Controlled growth of gallium nitride single-crystal nanowires using a chemical vapor deposition method

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Chemical vapor deposition (CVD) using gold nanoparticles as the catalyst to grow high-quality single-crystal gallium nitride nanowires was developed. This method enables control over several important aspects of the growth, including control of the nanowire diameter by using monodispersed gold clusters, control of the nanowire location via e-beam patterning of the catalyst sites, and control of the nanowire orientation via epitaxial growth on *a*-plane sapphire substrates. Our work opens up new ways to use GaN nanowires as nanobuilding blocks.

During the past few years, increasingly more effort has been devoted to the research on III–V nitride semiconductors because of their exciting properties.[1,2] GaN is particularly interesting among III–V nitrides, as its large band gap (3.4 eV), large dielectric breakdown field, superior electron transport properties, and good thermal conductivity make it ideal for high-power/high-temperature electronic applications. In addition, GaN is also used as an important optoelectronic material because of its direct band gap in the blue light-emitting regime. Success in growing high-quality GaN thin films has led to the demonstration of a family of novel devices such as blue light-emitting diodes,[3] laser diodes,[4] zero-dimension quantum dots,[5] and two-dimension quantum wells.[6,7] In contrast, controlled synthesis of GaN nanowires of predetermined diameters and/or at predetermined sites is still limited,[8,9] even though this can be important for nanoscale optoelectronic applications. Synthesis of GaN nanowires has been attempted by a number of groups using various techniques such as laser ablation of GaN-containing targets,[10,11] arc discharge,[12] nanotube-confined reaction of Ga/Ga_2O_3 with NH_3,[13] reaction of Ga/Ga_2O_3 mixture with NH_3 in anodic alumina templates,[14] and thermal chemical vapor deposition (CVD) from Ga-containing precursors and NH_3.[15–21] The laser ablation[10,11] and CVD[15–21] methods are particularly interesting because they exploit the vapor–liquid–solid (VLS) growth mechanism,[10] where In, Fe, Ni, and Co nanoparticles have been used as the catalyst. One common feature of the above-mentioned work is that growth of GaN nanowires of predetermined diameters has not been achieved, presumably because of the difficulty associated with producing monodispersed In, Fe, Ni, or Co nanoparticles. Monodispersed gold clusters are readily available; however, Duan *et al.* reported that no growth was observed when gold was used as the catalyst.[10] An additional common feature of previous work is that GaN nanowires were usually grown all over the surface and entangled together. Controlled growth of individual GaN nanowires at predetermined sites has not been demonstrated.

By using the CVD method with gold as the catalyst, significant control over several aspects of the synthesis of single-crystalline GaN nanowires is achieved, surprisingly. First of all, monodispersed gold clusters of well-defined diameters, in addition to thin gold films, were used as the catalyst particles, and this has allowed us to grow GaN nanowires of controlled diameters around 10, 20, and 30 nm. Second, controlled deposition of the gold clusters at desired sites on a substrate has been achieved via e-beam patterning, leading to the growth of GaN nanowires at desired sites. Finally, GaN nanowires were

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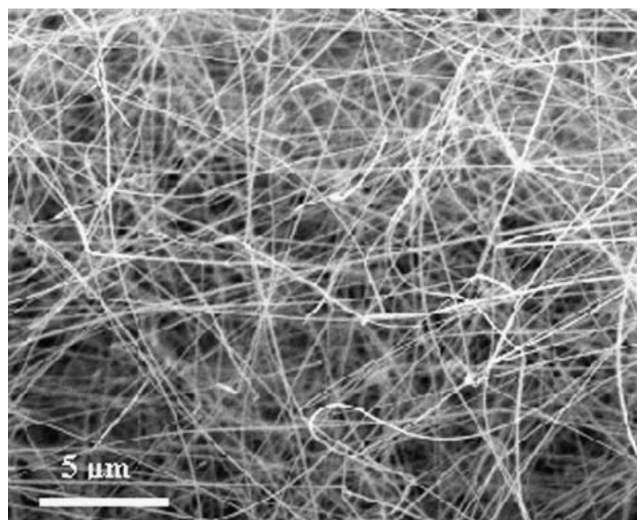
grown in near-vertical orientations on *a*-plane sapphire substrates by exploiting the epitaxial nature of the GaN/sapphire interface.

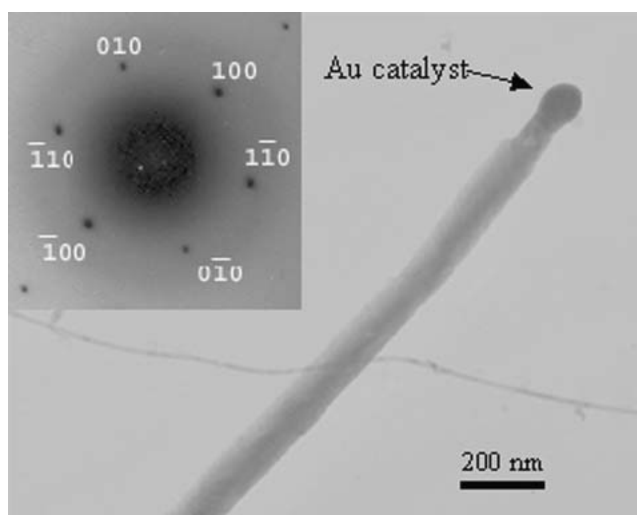
The preparation of the GaN nanowires is briefly described as follows. We first used a Si/SiO_2 substrate coated with 30-Å Au via e-beam evaporation, as such a thin film would form gold nanoparticles instead of a continuous film. This substrate was placed into a quartz tube at the downstream end of a furnace, and the gold nanoparticles were used as the catalytic particles for the GaN growth. The gallium source (99.9999%, Alfa Aesar, Ward Hill, WA) was placed upstream of the furnace. This quartz tube was heated to 900 °C, and the reaction was carried out by flowing anhydrous NH_3 gas through the quartz tube at 100 standard cubic centimeter per minute for typically about 10 min. After the system cooled, the Si/SiO_2 substrate was found to be coated with a layer of white material, which was confirmed to consist of GaN nanowires by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). Our synthesis is based on the VLS growth mechanism, where the Ga vapor first diffuses into the gold catalytic particles and grows out and reacts with NH_3 to form GaN once the Ga/Au alloy reaches supersaturation. Continued addition of Ga into the Ga/Au nanoparticle feeds the GaN growth, and hence, the diameter of the GaN nanowire should be directly linked to the catalytic particle size.

Figure 1(a) shows a typical SEM image of the high-yield GaN nanowires grown from the gold film. These nanowires covered the whole substrate and appeared to be homogeneous in the diameter. Detailed TEM and SEM examination show that these nanowires have diameters in the range 20–100 nm and lengths of tens of micrometers, indicating an aspect ratio exceeding 100:1. Figure 1(b) presents a detailed TEM examination of a single GaN nanowire, where the Au/Ga alloy particle can be clearly seen at the very tip of the nanowire, as a result of the VLS growth mechanism. This nanowire looks homogeneous and free of domain boundaries, indicating the single-crystalline nature of our material. The nanowire diameter is apparently consistent with the diameter of the catalytic particle, as expected from the VLS growth mechanism. The highly crystalline nature of our GaN nanowires was further confirmed by SAED. The Fig. 1(b) inset shows a SAED pattern, recorded perpendicular to the nanowire long axis. Detailed analysis of the diffraction pattern shows that our nanowire took the wurtzite structure and grew in the [100] direction with lattice constants $a = 3.178$ Å and $c = 5.120$ Å. These values are consistent with the values in the literature ($a = 3.18$ Å and $c = 5.16$ Å) for GaN materials.[1] We performed TEM examination and SAED over many nanowires and also at different locations along each nanowire. Similar diffraction patterns were always observed. The reason Duan *et al.* did not observe any growth with gold as the catalyst in their laser ablation approach[10] whereas we did is unclear at this moment. Since the VLS synthesis approach depends on a number of parameters such as the temperature, the pressure, the flow rate, and the detailed process of the chemical reaction, optimization of such growth conditions might very well lead to growth of GaN nanowires with gold as the catalyst even for the laser ablation approach.

Despite the above-mentioned success, direct and precise control over the GaN nanowire diameter is still highly desired because the electronic and optoelectronic properties of the nanowires are closely related to their



(a)



(b)

FIG. 1. (a) SEM image of GaN nanowires grown by the CVD technique on a SiO_2/Si substrate with 30-Å Au film used as the catalyst. The scale bar corresponds to 5 μm. (b) TEM image of a GaN nanowire grown with Au film showing the catalyst at the tip. The scale bar corresponds to 200 nm. Inset: SAED pattern of the GaN nanowire.

diameters.[22,23] We have achieved this by using monodispersed gold clusters of well-defined diameters instead of evaporated gold films as the catalysts. This represents a significant progress, compared to the lack of diameter control with the previously reported laser ablation method.[10] This is also made possible because gold clusters of well-defined diameters used in our growth are readily available, whereas it is significantly more difficult to make monodispersed iron clusters. Three types of gold clusters were used in our experiments, with diameters around 10, 20, and 30 nm, respectively. These nanoclusters were dispersed onto a Si/SiO_2 substrate following previously published work.[24] Polylysine (TED PELLA, Inc.) was first applied to a clean SiO_2 surface. After 5 min, the substrate was washed with D.I. (distilled deionized) water and then dried with N_2. Gold clusters were deposited onto the substrate by applying one drop of the cluster suspension, and the substrate was washed with D.I. water after 5 min and dried again. Oxygen plasma was used to clean up the polylysine left on the surface, and atomic force microscope images were taken to confirm a uniform distribution of Au clusters on the substrate, as shown in Fig. 2(a).

GaN nanowires were grown on the substrate decorated with gold clusters with the CVD method described above. Figure 2(b) shows a typical SEM image of the GaN nanowires synthesized this way. The diameters of nanowires are quite uniform, consistent with the VLS growth mechanism. The yield of nanowires is also consistent with the concentration of the gold clusters on the substrate. To further clarify this diameter-controlled growth we have carefully examined the diameters of more than 100 nanowires produced with each type of gold clusters with a transmission electron microscope. Histograms of the nanowire diameters are plotted in Figs. 3(c)–3(e) for gold clusters of 10, 20, and 30 nm,

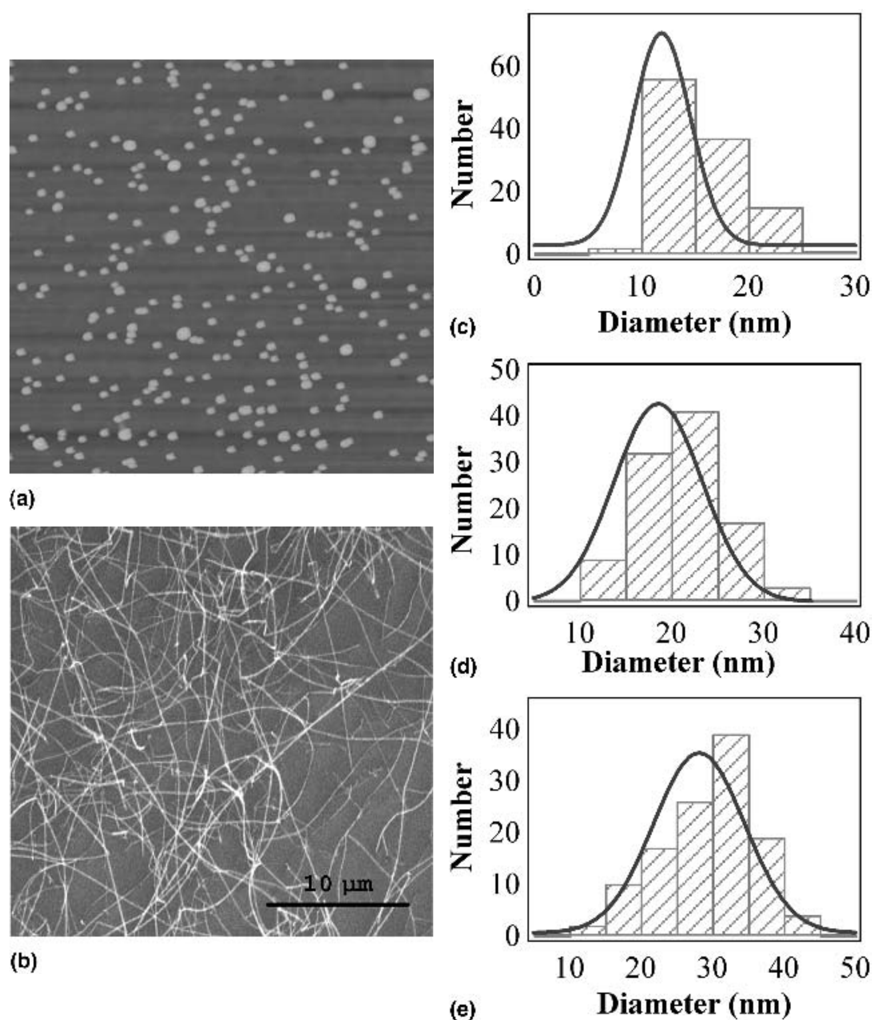


FIG. 2. (a) Atomic force microscope image of Au clusters (20 nm in diameter) on a SiO_2/Si substrate. The scan area is 4 μm × 4 μm. (b) SEM image of GaN nanowires grown by the CVD technique. The scale bar corresponds to 5 μm. (c–e) Histograms of GaN nanowire diameters grown from 10-, 20-, and 30-nm Au clusters, respectively.

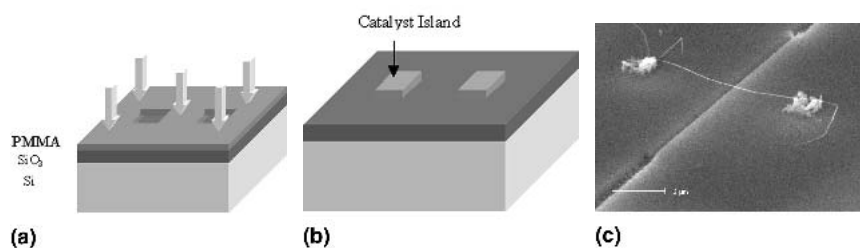


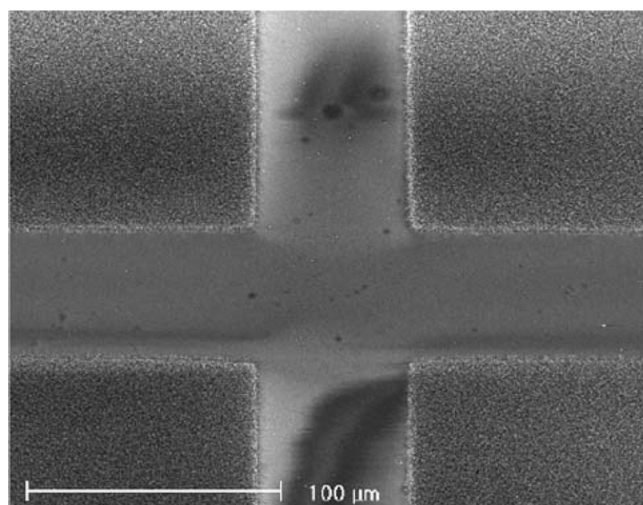
FIG. 3. Position-controlled growth of GaN nanowires: (a) catalyst suspension prepared by mixing 0.1 ml of Au cluster solution, 10 mg of alumina, and 20 ml of methanol and then deposited onto a e-beam patterned substrate; (b) lift-off performed to leave catalyst only in the patterned area; (c) SEM image of patterned growth of GaN nanowires. This nanowire lies across an etched trench and bridges two catalyst islands. The scale bar corresponds to 2 μm.

respectively. The distributions can be fitted with Gaussian curves, with average diameters at 11.9, 18.5, and 28.1 nm, respectively. This convincingly demonstrates the diameter-control capability of our method.

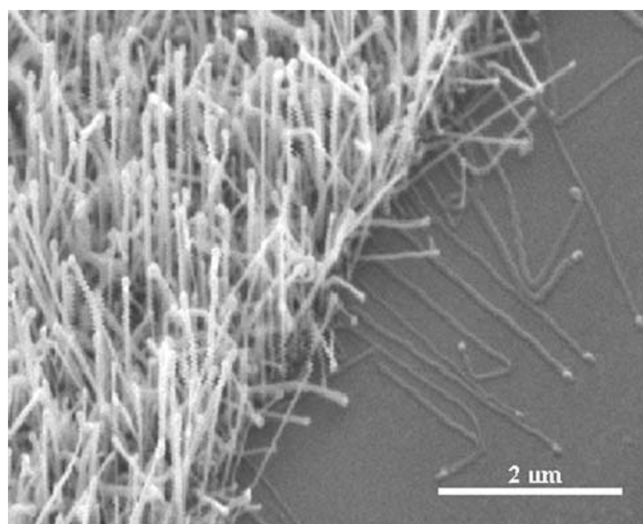
Armed with this diameter-controlled growth approach, we have also developed a method to grow GaN nanowires at desired sites on a substrate. This is achieved by patterning the gold catalytic clusters via e-beam lithography, as shown in Figs. 3(a) and 3(b). A SiO_2-coated silicon wafer was used as the substrate, and standard e-beam lithography was carried out to pattern two openings in a poly(methylmethacrylate) layer. Gold clusters and alumina particles were mixed into methanol to form a suspension, which was then deposited onto the patterned substrate. After the solvent evaporated, lift-off was carried out, leaving catalyst islands only in the pattern regions, as shown in Fig. 3(b). This substrate was then loaded into the CVD furnace, and the growth was performed. GaN nanowires were found to grow out of the catalyst islands and nowhere else, indicating gold clusters working as the seeds for growth. By controlling the concentration of the gold clusters in the methanol suspension, we have been able to control the yield of GaN nanowires, and very often we can get a single GaN nanowire between two adjacent catalyst islands, as shown in Fig. 3(c). This nanowire lies across a trench etched in the Si/SiO_2 substrate, which was designed for studies on the mechanical properties (such as bending) of the nanowires. The alumina particles were used to prevent the gold clusters from aggregating and also to produce a clean lift-off. This position-controlled growth is particularly important for making nanowire integrated systems since one does not need to locate the nanowires individually and many devices can be made in parallel on one chip by exploiting the advantage of batch processing. Compared with the previously reported microfluid method to position nanowires,[10] our method offers fast turnaround, is easy to use, and is fully compatible with the standard fabrication techniques. Electronic devices made via this position-controlled approach are currently under study and will be published elsewhere. A similar approach was developed for position-controlled growth of single-walled carbon nanotubes before and has since enabled the demonstration of many exciting nanotube devices and integrated systems.[25] We expect our position-controlled growth of GaN nanowires should have as much impact.

In addition to the diameter control and the position control, we have also attempted to control the nanowire to grow vertically on a suitable substrate, which is very important for optical and other applications.[26] Since GaN nanowires grow along the [100] direction, lattice match between the substrate surface and GaN *a* plane is crucial for the orientation control. *a*-plane sapphire, which also has wurtzite crystal structure, was chosen as the substrate for this purpose. The lattice constants of sapphire are $a = 4.758$ Å and $c = 12.991$ Å,[1] indicating a lattice mismatch about 13% between the substrate and GaN nanowires. The sapphire substrate was first carefully cleaned, and 30-Å Au was deposited onto the substrate with a TEM grid as the shadow mask. The CVD growth was performed using the above-mentioned method, and the reaction time was carefully controlled to produce nanowires of only several microns in length. Figure 4(a) shows a SEM image of the sample after the CVD growth. GaN nanowires were found to grow only out of the gold film region, as expected from the VLS growth mechanism. Figure 4(b) shows a magnified view of the as-grown GaN nanowires, and most of them can be seen in the vertical orientation. This clearly demonstrates the epitaxial nature between the sapphire substrate and the GaN nanowires; however, some nanowires are also found to grow along other directions, presumably because of the 13% lattice mismatch. More work is needed to gain full control over the GaN nanowire orientation, probably on substrates with smaller lattice mismatch.

To summarize, we have successfully developed a CVD technique to grow single-crystalline GaN nanowires using gold as the catalyst. By using monodispersed gold clusters as the catalyst, we are able to grow GaN nanowires with well-defined diameters. By combination of e-beam patterning with the CVD technique, GaN nanowires can be grown at desired sites, thus paving the way for further device fabrication and integration. By



(a)



(b)

FIG. 4. (a) SEM image of GaN nanowires grown from patterned catalyst on an *a*-plane sapphire substrate. The pattern was defined by using a TEM grid as a shadow mask during the gold film evaporation. (b) SEM image at high magnification showing most nanowires are in the vertical orientation. Some nanowires grew along the other direction presumably due to the lattice mismatch between the substrate and the nanowire.

using *a*-plane sapphire as the substrate, we have been able to grow the GaN nanowires mostly vertically. This method provides an easy way to grow GaN nanowires and could be extended to other nitride materials. GaN nanowires grown this way have great potential to be used for nanoscale electronic and optoelectronic devices.

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