Controlled Growth of Long GaN Nanowires from Catalyst Patterns Fabricated by "Dip-Pen" Nanolithographic Techniques

Jianye Li, Chenguang Lu, Benjamin Maynor, Shaoming Huang, and Jie Liu*

Department of Chemistry, Duke University, Durham, North Carolina 27708

Received June 12, 2003. Revised Manuscript Received August 21, 2003

Long gallium nitride (GaN) nanowires were directly grown on SiO_2 substrates from spatially defined locations using a chemical vapor deposition method. Locations of the GaN nanowires were well-controlled by using atomic force microscope (AFM)-based "dip-pen" nanolithography (DPN) and other patterning methods to precisely pattern catalyst islands on the substrate. Devices made of single GaN nanowires were fabricated and characterized. The convenient use of patterning techniques, especially the DPN technique, demonstrates a practical route to control the location of nanowires and for in situ fabrication of nanowire devices.

Introduction

The world of one-dimensional materials has presented exciting challenges for physicists, chemists, and materials scientists. The growth of one-dimensional materials has stimulated intensive research because of their ability to aid the understanding of basic concepts and their potential technological applications.[1] Wurtzite structure gallium nitride (GaN), a particularly important III−V semiconductor with a direct band-gap of 3.4 eV, is an ideal material for use as UV or blue photon emitters, photodetectors, high-speed field-effect transistors, and high temperature/high power electronic devices.[2−4] In the past few years, GaN one-dimensional structures, such as nanorods or nanowires, have attracted much attention because of their great potential for the new visible and UV optoelectronic applications.[5] Through a carbon-nanotube-confined reaction, Han et al. first demonstrated the synthesis of GaN nanorods.[6] Since this achievement, GaN nanowires or nanorods have been successfully synthesized and characterized by many groups.[5,7−14]

Nanowires with low defect density and long length are very important for preparation of nanoelectronic devices. Because the processing, dispersal, and patterning techniques, such as ultrasonication and lithography, can introduce defects in nanowires, growing nanowires suitable for in situ fabrication of nanowire devices represents a better method. To fabricate nanowire devices in situ, it is necessary to control the location and orientation of the nanowires. Therefore, patterning techniques must be developed that are capable of precisely delivering nanowire catalysts to desired locations. Recently, it was reported that Au catalysts patterned by electron-beam lithography technique can be used to grow GaN nanowires.[15] However, the electron-beam lithographic technique restricted the versatility of the technique. Meanwhile, it was recently demonstrated that an atomic force microscope (AFM)-based "dip-pen" nanolithography (DPN) technique was a very simple but powerful method to deposit various materials onto flat substrates.[16−19] Here, we report the use of the DPN technique and other patterning methods to conveniently pattern catalysts on a substrate for the controlled synthesis of GaN nanowires by chemical vapor deposition (CVD) growth. Using this procedure, we obtained long GaN nanowires at controlled locations. Use of these techniques, especially DPN, demonstrates a convenient approach to controlled growth of GaN nanowires for in situ fabrication of nanowire devices.

Experimental Section

The catalyst pattern was generated by direct photolithography, DPN, and macroscale writing techniques. For direct

* To whom correspondence should be addressed. E-mail: j.liu@duke.edu.

(1) Patzke, G. R.; Krumeich, F.; Nesper, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2446.
(2) Mohammad, N.; Morkoc, H. *Science* **1995**, *267*, 51.
(3) Fasol, G. *Science* **1996**, *272*, 175.
(4) Ponce, F. A.; Bour, D. P. *Nature* **1997**, *386*, 351.
(5) Chen, C. C.; Yeh, C. C.; Chen, C. H.; Yu, M. Y.; Liu, H. L.; Wu, J. J.; Chen, K. H.; Chen, L. C.; Peng, J. Y.; Chen, Y. F. *J. Am. Chem. Soc.* **2001**, *123*, 2791.
(6) Han, W.; Fan, S. H.; Li, Q. Q.; Hu, Y. D. *Science* **1997**, *277*, 1287.
(7) Duan, X. F.; Lieber, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 188.
(8) Chen, C. C.; Yeh, C. C. *Adv. Mater.* **2000**, *12*, 738.
(9) Chen, X. L.; Li, J. Y.; Cao, Y. G.; Lan, Y. C.; Li, H.; He, M.; Wang, C. Y.; Zhang, Z.; Qiao, Z. Y. *Adv. Mater.* **2000**, *12*, 1432.
(10) Tang, C. C.; Fan, S. S.; Dang, H. Y.; Li, P.; Liu, M. Y. *Appl. Phys. Lett.* **2000**, *77*, 1961.
(11) He, M. Q.; Minus, I.; Zhou, P. Z.; Mohammed, S. N.; Halperm, J. B.; Jacobs, R.; Sarney, W. L.; Salamanca-Riba, L.; Vispute, R. D. *Appl. Phys. Lett.* **2000**, *77*, 3731.
(12) Han, W. Q.; Zettl, A. *Appl. Phys. Lett.* **2002**, *80*, 303.
(13) Seo, H. W.; Bae, S. Y.; Park, J.; Yang, H. N.; Park, K. S.; Kim, S. *J. Chem. Phys.* **2002**, *116*, 9492.
(14) Kim, H. M.; Kim, D. S.; Park, Y. S.; Kim, D. Y.; Kang, T. W.; Chung, K. S. *Adv. Mater.* **2002**, *14*, 991.
(15) Han, S.; Jin, W.; Tang, T.; Li, C.; Zhang, D.; Liu, X.; Han, J.; Zhou, C. W. *J. Mater. Res.* **2003**, *18*, 245.
(16) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661.
(17) Li, Y.; Maynor, B. W.; Liu, J. *J. Am. Chem. Soc.* **2001**, *123*, 2105.
(18) Maynor, B. W.; Li, Y.; Liu, J. *Langmuir* **2001**, *17*, 2575.
(19) Demers, L. M.; Ginger, D. S.; Park, S. J.; Li, Z.; Chung, S. W.; Mirkin, C. A. *Science* **2002**, *296*, 1836.

10.1021/cm0344764 CCC: $27.50 © 2004 American Chemical Society
Published on Web 03/20/2004

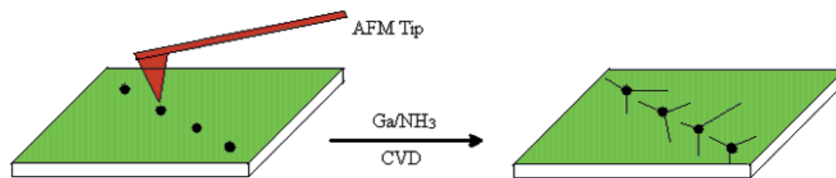


Figure 1. Schematic of the DPN process for the patterning of catalysts and growth of GaN nanowires.

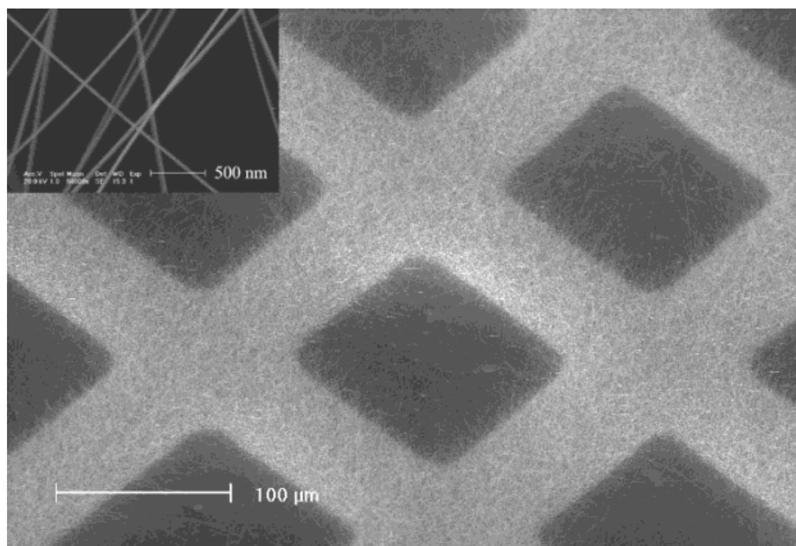
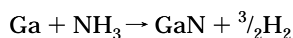


Figure 2. FESEM images of GaN nanowires after in situ growth on a polished silicon wafer (100-nm-thick thermal oxide). The wafer was photolithographically patterned with iron(III) acetylacetonate.

photolithography, iron(III) acetylacetonate was used as catalyst precursor and DNQ Novolak resin was used as the photoresist.[20,21] DPN patterning of catalysts was performed on a Digital Instruments Nanoscope IIIa/MultiMode AFM. In a typical experiment, a contact-mode AFM tip (Digital Instruments NP-20) was dip-coated with a $Ni(NO_3)_2$ solution and dried with fluorocarbon gas. The tip was then brought into contact with the substrate under controlled humidity to precisely deliver a small amount of $Ni(NO_3)_2$ as demonstrated in a sketch shown in Figure 1. The position of catalyst islands was controlled by moving the tip from location to location using the piezoelectric scanner, with tip dwell time ranging from 30 s to 2 min.

To synthesize GaN nanowires, elemental gallium and ammonia were used as starting materials. They react according to the following scheme:



$$Ga + NH_3 \rightarrow GaN + {}^3/_2H_2$$

Preparation of the GaN nanowires was as follows. The growth was carried out in a horizontal quartz tube inside a tube furnace. Elemental gallium (99.999%, Alfa Aesar) and catalyst-patterned substrates with a separation of 3−10 cm were loaded into an alumina boat and placed at the center of the horizontal quartz glass tube. The quartz tube was heated under a flow of argon of about 600 cm^3 per minute to allow degassing of the tube. The furnace temperature was then raised to 920−960 °C, and a flow of ammonia (99.99%, National Specialty Gases) of about 30−60 standard cubic centimeters per minute (sccm) was initiated. After 2−3 h, the furnace was switched off and allowed to cool to room-temperature quickly. To protect the as-grown GaN nanowires from decomposition, the flow of ammonia was maintained during the cooling process.

The morphologies of the as-formed samples were characterized by field emission scanning electron microscopy (FESEM; Philips FEI XL30SFEG). The crystal structure and phase purity of the products were characterized using X-ray powder diffraction (XRD; Rigaku Multiflex X-ray diffractometer with Cu Kα radiation at room temperature).

Results and Discussion

Transition metal oxides such as nickel and iron oxide are known to catalyze GaN nanowire growth by the vapor−liquid−solid (VLS) mechanism.[9] In this report, nickel(II) oxide and iron(III) oxide were used as the catalysts for nanowire growth. For catalyst patterning, nickel(II) nitrate and iron(III) acetylacetonate were used as the catalyst precursors. At high temperature, nickel(II) nitrate and iron(III) acetylacetonate decompose to produce NiO and Fe_2O_3.

Because the catalyst precursors are simple metal salts and can be dissolved in water and other solvents, they can be patterned by standard microlithography techniques such as photolithography. Figure 2 shows FESEM images of GaN nanowires controllably grown from photolithographic-patterned iron(III) acetylacetonate on a silicon wafer with 100-nm-thick thermal oxide. As shown in Figure 2, patterns of GaN nanowires were observed after CVD growth. The inset of Figure 2 shows the high-magnification FESEM image of the GaN nanowires. Most of the nanowires have diameters in the range of 10−50 nm. The nanowires are straight and smooth, indicating the crystalline and uniform structure of the materials.

X-ray diffraction measurements were performed on bulk samples to assess the overall crystal structure and phase purity of the product. Figure 3 shows a typical powder XRD spectrum of the patterned GaN nanowires shown in Figure 2. The diffraction peaks in the XRD spectrum were indexed to a hexagonal wurtzite struc-

(20) Huang, S. M.; Dai, L. M.; Mau, A. W. H. *Adv. Mater.* **2002**, *14*, 1140.
(21) Huang, S. M.; Mau, A. W. H.; Turney, T. W.; White, P. A.; Dai, L. M. *J. Phys. Chem. B* **2000**, *104*, 2193.

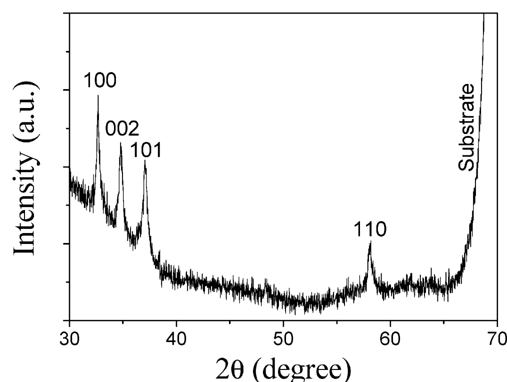
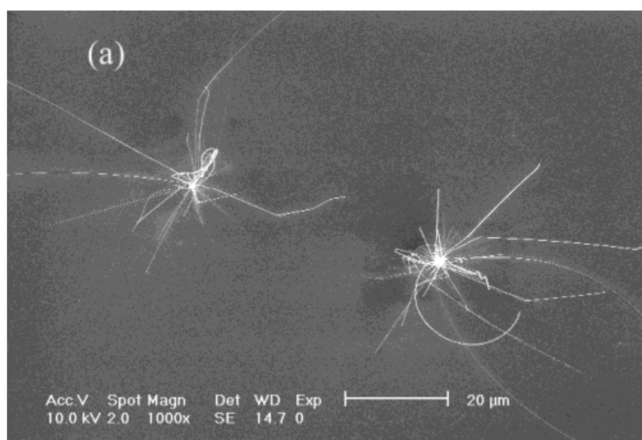


Figure 3. Room-temperature XRD of GaN nanowire patterns on a silicon wafer (polished silicon with 100-nm-thick thermal oxide) using Cu Kα radiation.



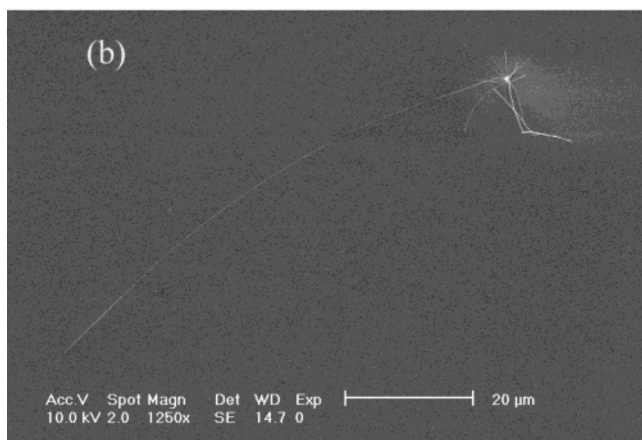


Figure 4. FESEM images of (a) GaN nanowires controllably grown from DPN patterned catalyst sites on polished silicon with 1000-nm-thick thermal oxide, and (b) long GaN nanowires grown on a DPN patterned catalyst site.

ture of GaN. These data are in good agreement with the reported values of hexagonal GaN with lattice constants of $a = 0.3186$ nm and $c = 0.5178$ nm.[22] The presence of strong diffraction peaks relative to the background signal suggests that the nanowire products have a highly pure hexagonal wurtzite GaN phase.

For future in situ fabrication of GaN nanoscale devices from nanowires directly grown on suitable substrates, the capability to pattern the catalysts with higher resolution using simple patterning techniques is

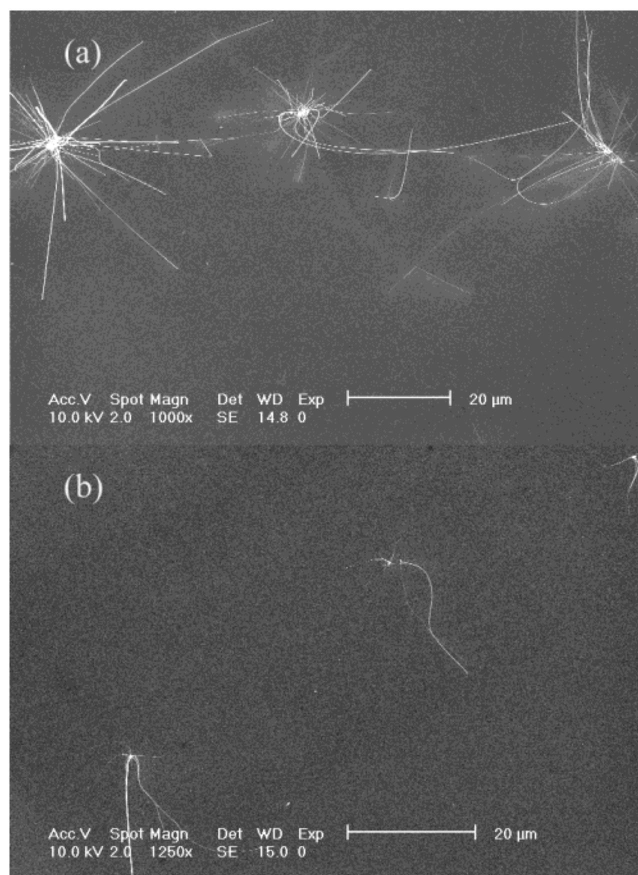


Figure 5. FESEM images of GaN nanowires controllably grown from the catalyst sites patterned by DPN at (a) higher, and (b) lower humidity.

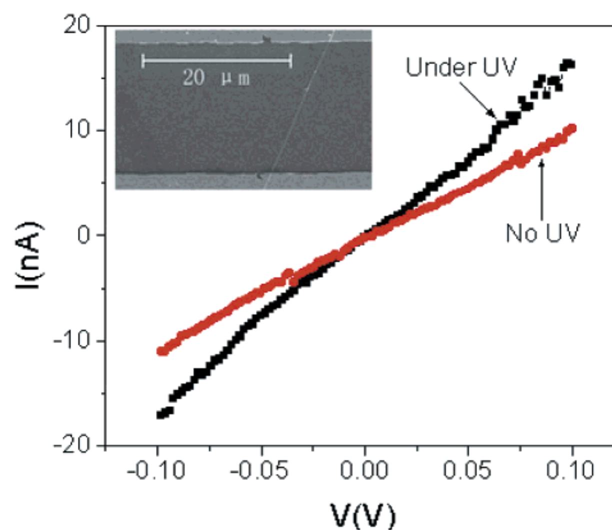


Figure 6. Room-temperature $I-V$ curves of the single wire device with and without UV illumination. Inset: FESEM image of an individual GaN nanowire device.

critical. One suitable technique is DPN, an AFM-based lithography technique capable of fabricating nanometer- and micrometer-size features directly on substrates.[16-19] The combination of DPN and GaN nanowire growth is especially desirable because of the higher growth efficiency of GaN nanowires compared to other one-dimensional systems, such as carbon nanotubes. In the case of carbon nanotubes, although catalysts can be patterned using DPN, the growth yield is so low that it is hard to grow nanotubes from every catalyst island.

(22) JCPDS International Center for Diffraction Data, Card 02-1078, 1997.

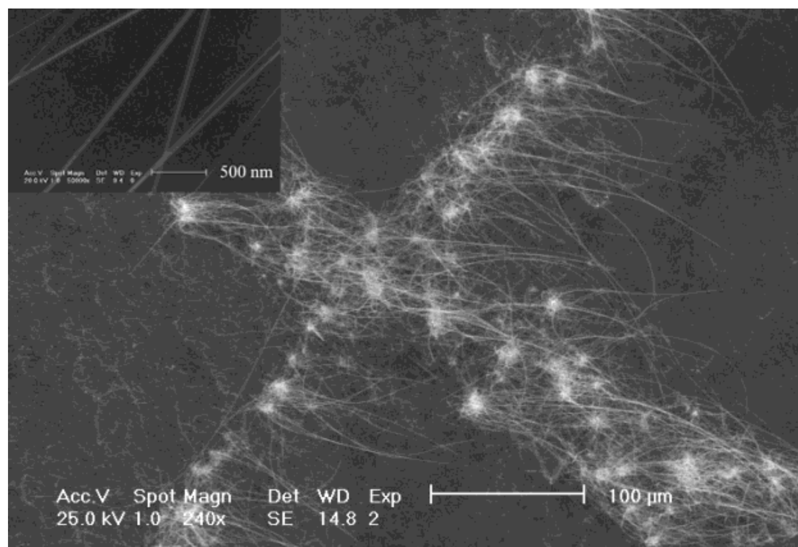


Figure 7. FESEM image of the long GaN nanowires deposited on the top of unpolished silicon with 1000-nm-thick thermal oxide. The patterning of catalysts was written using a sharp iron needle coated with nickel oxide precursor by dipping into a 0.01 M $Ni(NO_3)_2$ solution in methanol.

GaN nanowires do not have this problem. As shown in Figure 4, GaN nanowires can be controllably grown from each DPN patterned catalyst island. Figure 4(a) shows FESEM images of GaN nanowires synthesized from DPN patterned catalyst sites and Figure 4(b) is a FESEM image of a long GaN nanowire (90 μm) grown on a DPN patterned catalyst site. It can be seen from Figure 4 that the nanowires are smooth and have diameters ranging from 10 to 60 nm. To the best of our knowledge, this is the first demonstration of using DPN to produce patterned catalyst islands for the in situ growth of nanowires. The capability to grow GaN nanowires at specific locations makes the future fabrication of nanowire devices a more convenient process.

Patterning of catalysts on substrate using DPN is a critical step in our experiments. When the coated tip is engaged with the surface, the $Ni(NO_3)_2$ diffuses away from the AFM tip to the surface through the condensed water meniscus between the tip and the substrate. The size of the catalyst islands is related to the humidity, the shape of the AFM tip and dwell time; and the morphologies as well as the total number of nanowires from each catalyst island are related to the catalyst island size. Figure 5 shows the images of GaN nanowires grown from the catalyst sites patterned by DPN at different humidity while keeping all other conditions the same. It clearly shows the effect of humidity during pattering on the total number of nanowires grown from each catalyst island. More systematic studies are underway in our group for more precise control of the size of the catalyst islands.

To test the electronic properties of individual GaN nanowires, devices were prepared by evaporating metal electrodes on the nanowires. Figure 6 shows the room-temperature $I-V$ curves of the device measured with and without shortwave UV light (254 nm) illumination. As is expected for semiconducting GaN, under UV illumination the conductivity of the nanowire increases distinctly. The inset shows the SEM image of the GaN nanowire device. The diameter of the nanowire is about 60 nm.

Last, we have found that it is possible that the horizontal orientation of GaN nanowires could be controlled by the flow of feeding gas in the CVD chamber. As shown in Figure 7, GaN nanowires grown from patterned catalysts have shown a trend of alignment, especially when the nanowires are long (~100 μm). We have found that the alignment direction was the same as the direction of gas flow in the growth chamber. The length of the nanowires can be over 100 μm under the current growth conditions. However, the degree of alignment is still not satisfactory for device fabrication. More research is needed to introduce better alignment.

Conclusions

In summary, long GaN nanowires were synthesized on DPN-generated catalyst islands at precisely controlled locations using a simple CVD growth process. The simplicity of the DPN technique and the capability to perform parallel patterning using a multi-pen, large-scale approach as demonstrated by the Mirkin Group [23,24] makes it potentially useful for the fabrication of precisely patterned catalyst islands over large areas. SEM images demonstrated that these nanowires were very long, smooth, and straight, and XRD analysis revealed that they possess a GaN wurtzite crystal structure. Device fabrication and characterization were demonstrated. Currently, nanowire devices are predominantly fabricated using labor-intensive electron-beam lithography. The capability of precisely controlling the locations of nanowires over large areas paves the way for fabrication of nanowire devices using conventional photolithographic patterning on a large scale.

Acknowledgment. This work is supported in part by Grant 49620-02-1-0188 from AFOSR and the Army Research Office (Grant 2000-ARG-0041). The authors acknowledge Professor Gleb Finkelstein for the use of the SEM.

CM0344764

(23) Hong, S. H.; Zhu, J.; Mirkin, C. A. *Science* **1999**, *286*, 523–525.
(24) Lee, K. B.; Park, S. J.; Mirkin, C. A.; Smith, J. C.; Mrksich, M. *Science* **2002**, *295*, 1702–1705.