Low-Temperature Catalytic Synthesis of Gallium Nitride Nanowires

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Catalytic growth of high-purity GaN nanowires is achieved at temperatures of 750 and 620 °C using gallium acetylacetonate and ammonia gas. The straight single-crystal GaN nanowires with diameters in the range 15−60 nm are found to grow following the vermicular-like nanowires on Si(100) substrate at 750 °C via a vapor−liquid−solid (VLS) mechanism using Ni as a catalyst. Photoluminescence (PL) characteristics of the GaN nanowires show a UV emission peak ranging from 360 to 420 nm at room temperature. Successful growth of GaN nanowires at low temperatures is suggested to be due to sufficient gallium precursor provided by gallium acetylacetonate during synthesis.

Introduction

One-dimensional nanostructures have great potential for learning the fundamental concepts of the roles of both dimensionality and size in the physical properties, as well as for application in nanodevices and functional materials.[1] Because of its wide band gap property (3.4 eV at room temperature) promising for blue and ultraviolet optoelectronic nanodevices, many reach efforts have been devoted to synthesize single-crystal GaN nanowires. The growth of GaN nanowires has been demonstrated by various high-temperature methods, such as the template-based growth methods,[2] the vapor−liquid−solid (VLS) mechanism,[3] and the native nanocrystal-seeded method.[4] Among them, the synthesis temperatures are all above 850 °C. In contrast to Ga organometallic precursors popularly used for GaN film deposition,[5] Ga or Ga_2O_3 was usually employed to be Ga source for GaN nanowire growth. Recently, the catalytic growth of GaN nanowires using organometallic precursors including Ga (gallium dimethylamide) and catalyst (ferrocence) sources has been reported.[6] However, carbon nanotubes are present with GaN nanowires in the products at process temperatures of 900 and 1000 °C. For low-temperature growth of GaN nanowires, we suggest that a Ga source for providing sufficient precursor is crucial in addition to selection of a proper catalyst for the VLS mechanism proceeding at low temperatures. Here, we demonstrate the synthesis of GaN nanowires on Ni-pretreated Si substrates via the VLS mechanism at temperatures lower than those that have been reported using ammonia gas and a gallium organometallic compound, gallium acetylacetonate, with a low decomposition temperature (∼196 °C). Structural characterization of the GaN nanowires by transmission electron microscopy (TEM) shows that straight single-crystal GaN nanowires grew following vermicular-like bases at 750 and 620 °C. Photoluminescence (PL) characteristics of the GaN nanowires show a UV emission peak ranging from 360 to 420 nm at room temperature.

Experimental Section

GaN nanowires were synthesized in a 3" quartz tube inserted into a two-temperature-zone furnace. Silicon substrates were dipped with 0.01 M of $Ni(NO_3)_3$ solution after being cleaned in an ultrasonic bath of acetone for 20 min. Gallium acetylacetonate (($(CH_3COCHCOCH_3)_3Ga$, Aldrich, 99.99%) placed on a cleaned Pyrex glass container was loaded into the low-temperature zone of the furnace. The base pressure of the quartz reactor was 5×10^{-3} Torr. During synthesis, the low-temperature zone was controlled to be at a temperature of 130−185 °C to vaporize the solid source. The vapor was carried by a 100 sccm NH_3 flow into the higher temperature zone in which Si substrate pretreated with Ni catalyst was located at 200 Torr. The distance between the Ga source and the substrate is 25−30 cm. The morphology and size distribution, as well as elemental analysis of the nanowires, were examined using scanning electron microscopy (SEM, Hitachi, S-4200), which was equipped with an energy dispersive spectroscopy (EDS). The crystal structure of the nanowires was analyzed using transmission electron microscopy (JEOL 2010 and JEM-4000EX). Photoluminescence studies were conducted with a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp at room temperature. The excitation wavelengths were 325 and 254 nm.

Results and Discussion

As the vaporizing temperature of the gallium acetylacetonate was set to be at 185 °C, light yellow products were formed on Ni-catalyst-treated Si substrates at 750 °C. Wire-like morphology of the light yellow products synthesized for 6 h is distributed uniformly over the entire Si substrate from SEM observation. As shown in Figure 1a, rather straight nanowires were formed with diameters in the range 15−60 nm and with lengths of several tens of micrometers after 6 hours of growth. EDS analyses show that the nanowires are composed of Ga and N elements. Figure 1b illustrates the morphology of the GaN nanowires grown for 30 min. In addition to the straight nanowires, vermicular-like nanowires are also observed right on the surface of the substrate after 30 min of growth. As shown in Figure 1b, the straight nanowire is connected with the vermicular-like nanowire, suggesting that the vermicular-like structure grew in the early stage at 750 °C and then the straight GaN nanowire was formed following it. The nanoparticle at the top of the GaN nanowire, as marked by an arrow in Figure 1b, indicates the formation of the nanowires via the VLS mechanism. The growth of GaN nanowires at a lower temper-

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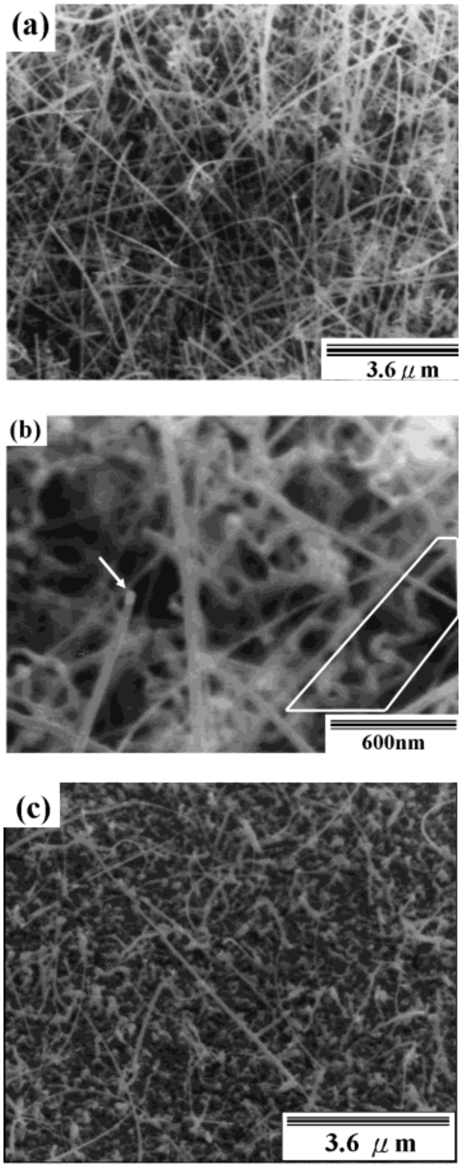

Figure 1. SEM images of GaN nanowires grown at (a) 750 °C for 6 h, (b) 750 °C for 30 min, and (c) 620 °C for 6 h.

ature of 620 °C has been achieved using gallium acetylacetonate source at a vaporizing temperature of 130 °C. As shown in Figure 1c, needlelike GaN nanowires with short vermicular-like structures were formed on the substrate. In comparison with those grown at 750 °C shown in Figure 1a, the density of the straight nanowires is reduced as growth temperature is lowered to 620 °C.

The microstructure of the GaN nanowires grown at 750 °C was characterized using high-resolution (HR) TEM. It should be noted here that no carbon nanotube is observed in the products from TEM analyses although the Ga source contains carbon element, indicating the synthesis of high-purity GaN nanowires has been achieved using gallium acetylacetonate. Figure 2a shows a low-magnification TEM image of an individual nanowire that consists of straight and vermicular-like parts. It confirms the SEM observation that the straight nanowires are grown following the vermicular-like base. The HRTEM image of the bottom portion of the nanowire, as marked by an arrow in Figure 2a, is shown in Figure 2b. The high-resolution image reveals that the vermicular-like nanowire possesses crystalline structure and several dislocation defects appear within the highly curved portion of the nanowire. Figure

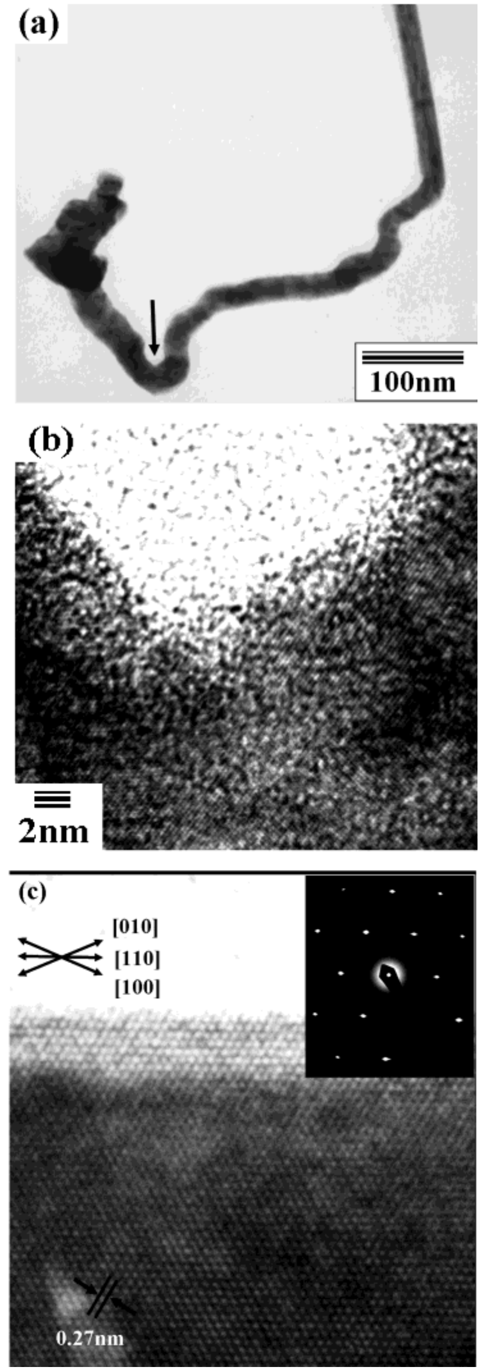

Figure 2. Low-magnification TEM image (a) of the GaN nanowire grown at 750 °C; (b) HRTEM image of the bottom portion of the nanowire, as marked by an arrow in panel a; (c) HRTEM image of the straight portion of the nanowire and the corresponding electron diffraction pattern (inset).

2c shows a HRTEM image of the straight portion of the nanowire, as well as the corresponding electron diffraction pattern (inset). The diffraction pattern indicated that the GaN nanowire exhibits a hexagonal structure. The lattice spacing of 0.27 nm, as shown in the HRTEM image, corresponds to the d spacing of (100) crystal planes of the hexagonal GaN. The [110] direction is parallel to the longitudinal axis of the nanowire, indicating that the fast-growth direction is along the [110] direction of the GaN nanaowire in this case. The fast-growth directions along the [100] and [103] directions are also observed from HRTEM analyses of the GaN nanaowires synthesized in this study.

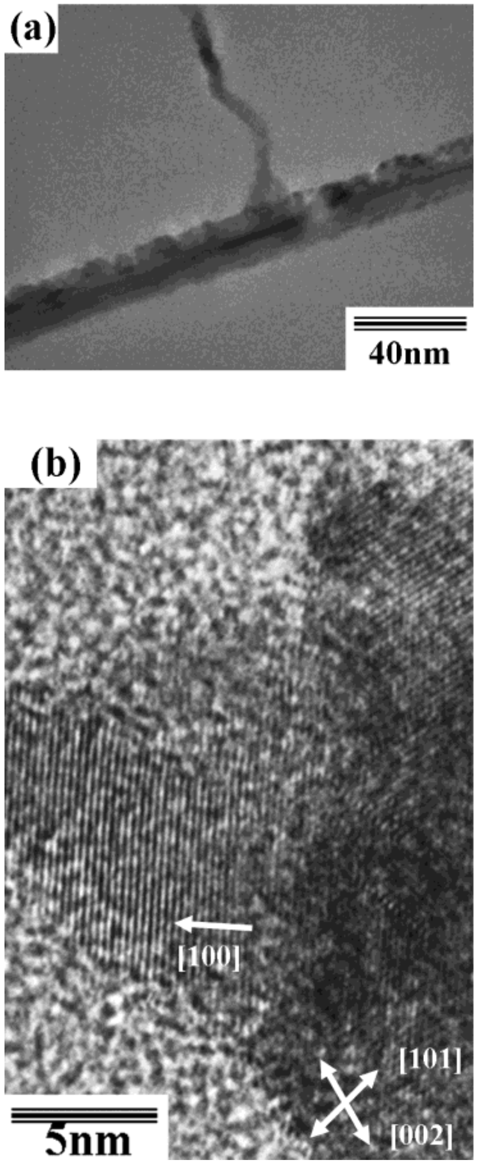

Figure 3. TEM image (a) of the branching GaN nanowire; (b) HRTEM image of the T-junction portion of the branching GaN nanowire.

In addition to 1-D GaN nanowires, nanowires with a branching configuration have been also observed from HRTEM, as shown in Figure 3a. The HRTEM image of the T junction portion, as illustrated in Figure 3b, shows the lattice planes of both the bough and the twig of the branching GaN nanowire. However, the nonconsistence of lattice directions of the bough and the twig suggests that the twig was grown originating from a defect of the bough of the branching GaN nanowire.

PL measurements of the GaN nanowire were carried out using a fluorescence spectrophotometer with a Xe lamp. Figure 4a shows the PL spectrum of the GaN nanowires synthesized at 750 °C with an excitation wavelength of 254 nm. A broad emission band ranging from 360 to 420 nm was observed in this spectrum. The broad emission band shown in Figure 4a might be ascribed to the band edge emissions of both the hexagonal-structured GaN nanowires and the cubic-phase-structured GaN. The cubic GaN structure, of which the band edge emission is at 3.2 eV,[7] could exist within the highly curved portion of the vermicular-like structures as stacking faults.[8] To examine the yellow defect band emission of the GaN nanowires that is observed from almost all samples of GaN films and nanowires,[9] the excitation wavelength was varied from 254 to 325 nm to avoid the secondary line of 254 nm excitation. As shown in Figure 4b, yellow luminescence also appears in the spectrum of the GaN nanowires synthesized at 750 °C. In additions, emission bands centered at around 450 and 470 nm are observed in both spectra a and b. The observation of these emission bands of GaN nanowires has been suggested to be the contributions of the existence of defect or surface states.[10] However, the mechanism of these emissions is not yet clear.

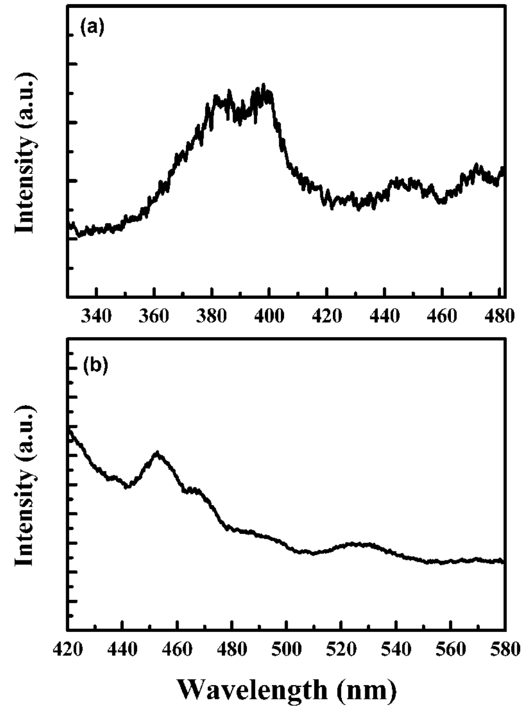

Figure 4. PL spectra of the GaN nanowires with an excitation wavelength of (a) 254 and (b) 325 nm.

In addition to selection of a proper catalyst for the VLS mechanism proceeding at low temperatures, we suggest that having sufficient precursors is another crucial point for low-temperature growth of nanowires via the VLS method. In the case of VLS−GaN nanowires synthesized using Ga metal, the Ga source is heated together with catalyst-pretreated substrates at a temperature higher than 850 °C and nanowires are formed on the substrates at a position near the source. The product with desired morphology, as well as diameter, is obtained only within a very narrow region.[8,11] This implies that the reactant depletion problem could be a concern in the growth of GaN nanowires using Ga metal because of the low vapor pressure of Ga metal ($\sim 10^{-4}$ Torr at 900 °C[12]). In contrast to Ga metal, the low decomposition temperature (∼196 °C) of the organometallic source of gallium acetylacetonate can provide more sufficient Ga vapor than can Ga metal. By employing a two-temperature-zone furnace operated at low pressure, the concentration of Ga precursor can be controlled by the temperature of the low-temperature zone, which is independent of the temperature for GaN nanowire growth in the second zone. The concentration of the Ga precursor would not be decreased as the substrate temperature is lowered in contrast to the case of Ga metal. Thus, the possibility that the catalyst would form a miscible liquid phase with Ga and N remains the only restriction for low-temperature growth of GaN nanowires. It has been achieved in this work that the GaN nanowires can be synthesized at a temperature as low as 620 °C using Ni as a catalyst under the condition with sufficient precursors.

Conclusions

This work demonstrates the catalytic growth of high-purity GaN nanowires using gallium acetylacetonate and ammonia gas at temperatures of 750 and 620 °C, which are lower than those that have been reported for GaN nanowires growth. The straight single-crystal GaN nanowires with diameters in the range 15–60 nm are found to grow following the vermicular-like nanowires at 750 °C using Ni as a catalyst. Branching GaN nanowires are also observed in the products. Photoluminescence (PL) characteristics of the GaN nanowires show a UV emission peak ranging from 360 to 420 nm at room temperature. We suggest that sufficient Ga precursor provided by gallium acetylacetonate is crucial in addition to selection of a proper catalyst for the VLS mechanism proceeding at low temperatures.

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References and Notes

(1) Lieber, C. M. *Solid State Commun.* **1998**, *107*, 607.

(2) (a) Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997**, *277*, 1287. (b) Cheng, G. S.; Zhang, L. D.; Zhu, Y.; Fei, G. T.; Li, L. *Appl. Phys. Lett.* **1999**, *75*, 2455. (c) Cheng, G. S.; Chen, S. H.; Zhu, X. G.; Mao, Y. Q.; Zhang, L. D. *Mater. Sci. Eng. A* **2000**, *286*, 165.

(3) (a) Duan, X.; Lieber, C. M. *J. Am. Chem. Soc*. **2000**, *122*, 188. (b) Chen, C.-C.; Yeh, C.-C. *Adv. Mater*. **2000**, *12*, 738. (c) Peng, H. Y.; Zhou, X. T.; Wang, N.; Zheng, Y. F.; Liao, L. S.; Shi, W. S.; Lee, C. S.; Lee, S. T. *Chem. Phys. Lett*. **2000**, *327*, 263. (d) 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.

(4) He, M.; Minus, I.; Zhou, P.; Mohammed, S. N.; Halpern, J. B.; Jacobs, R.; Sarney, W. L.; Salamanca-Riba, L.; Vispute, R. D. *Appl. Phys. Lett.* **2000**, *77*, 3731.

(5) Strite, S.; Morkoc, H. *J. Vac. Sci. Technol. B* **1992**, *10*, 1237.

(6) Han, W.-Q.; Zettl, A. *Appl. Phys. Lett.* **2001**, *80*, 303.

(7) Okumura, H.; Hamaguchi, H.; Feuillet, G.; Ishida, Y.; Yoshida, S. *Appl. Phys. Lett.* **1998**, *72*, 3056.

(8) 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.

(9) (a) Suski, T.; Perlin, P.; Teisseyre, H.; Leszczynski, M.; Grzegory, I.; Jun, J.; Bockowski, M.; Porowski, S.; Moustakas, T. D. *Appl. Phys. Lett.* **1995**, *67*, 2188. (b) Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997**, *277*, 1287. (c) Chen, C.-C.; Yeh, C.-C. *Adv. Mater*. **2000**, *12*, 738.

(10) Chen, X.; Li, J.; Cao, Y.; Lan, Y.; Li, H.; He, M.; Wang, C.; Zhang, Z.; Qiao, Z. *Adv. Mater.* **2000**, *12*, 1432.

(11) Li, Z. J.; Chen, X. L.; Li, H. J.; Tu, Q. Y.; Yang, Z.; Xu, Y. P.; Hu, B. Q. *Appl. Phys. A* **2001**, *72*, 629.

(12) Honig, R. E.; Kramer, D. A. *RCA Rev.* **1969**, *30*, 285.