Excellent Field-Emission Properties of P-Doped GaN Nanowires

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GaN nanowires with P doping were synthesized via a simple thermal evaporation process. The P-doped GaN nanowires have average diameters of ∼100 nm and lengths up to tens of micrometers. Scanning electron microscope and high-resolution field-emission transmission electron microscope analyses revealed that P doping results in a rough surface morphology of GaN nanowires. Field-emission measurements showed that P doping effectively decreases the turn-on field of GaN nanowire to 5.1 V/μm, holding promise of application as an electron emitter. The rough surface is responsible for enhancement of the field-emission properties of GaN nanowires.

Introduction

Doping of semiconductors with impurity elements has been a feasible way in tuning their electronic properties to meet the requirements for device fabrication. From a fundamental research point of view it is also of interest to understand the basic concept and intriguing phenomena.[1] Due to their intriguing properties and technological applications, GaN alloys doped with various impurity elements, such as Si, Mg, Al, Mn, etc., have received tremendous attention.[2−6] Further, it is also easy to incorporate these impurity elements into GaN because of the possibility of lattice matching.[4]

As an important semiconductor material $GaN_{1-x}P_x$ ternary alloy has potential applications in photonic and electronic devices operating in the wide visible wavelength range due to its gigantic band-gap bowing.[7] Despite the technological importance for $GaN_{1-x}P_x$ semiconductor, little has been reported for P doping in GaN due to the lattice mismatch between hexagonal GaN and cubic GaP as well as the large miscibility gap, which leads to the difficult preparation of the $GaN_{1-x}P_x$ samples.[8] After the discovery of carbon nanotubes, GaN nanostructured materials with various morphologies such as nanowires, nanobelts, and nanotubes have received much attention due to their potential applications in short-wavelength optoelectronic devices.[9−13] However, doping for nanoscaled GaN still remains a challenge because of the difficult implantation of impurity elements. In this paper we report the doping of P in GaN nanowires and the related field-emission behavior.

Experimental Section

The GaN nanowires with/without P doping are synthesized via a simple thermal evaporation process. Ga_2O_3:GaN (2:1 mol/mol) or Ga_2O_3:GaN:InP (20:10:1 mol/mol/mol) powders (Wako; Ga_2O_3, 99.99%, 1 μm; GaN, 99.99%, 1 μm; InP, 99.99%) were mixed uniformly and then loaded into a Al_2O_3 boat covered with Si (111) substrate coated with Au film (5 nm in thickness). The Al_2O_3 boat was placed into the center of a quartz tube and heated in a conventional horizontal resistance furnace. The whole reaction system was first heated to 1023 K in the protection of flowing Ar with a rate of 200 mL/min, and NH_3 gas with a rate of 300 mL/min was introduced to replace Ar gas as the temperature was increased to 1423 K. After reacting for 30 min the system was cooled to room temperature in Ar flow; a layer of slightly yellow powder densely growing on Si substrate with an area of 15 × 15 mm^2 was collected and examined by an X-ray diffractometer (XRD, RINT-2200V, 40 V/40 mA with Cu K_α radiation), a scanning electron microscope [(SEM) JEOL, JSM-6700F], and a high-resolution field-emission transmission electron microscope [(TEM) JEOL, JEM-3000F] equipped with an X-ray energy dispersive spectrometer (EDS). Field-emission (FE) measurements for the as-synthesized products were conducted in a vacuum chamber at a pressure of 2 × 10^{-6} Torr at room temperature.

Result and Discussion

Figure 1a and b show the representative SEM image for the GaN nanowires with P doping. A low-magnification SEM image for GaN nanowires without P doping is shown in Figure 1c for comparison with the effect of P doping on the morphology. It could be seen that the morphologies of GaN nanowires with/without P doping display an obvious difference. Typically the undoped GaN nanowires are straight and have a relatively smooth surface as highlighted by the representative SEM image for an individual GaN nanowire shown in the inset of Figure 1c, whereas the P-doped GaN nanowires are curved and densely covered on the Si substrate. Importantly, the surfaces of the doped GaN nanowires are considerably rough, and some particles tens of nanometers in size could also be easily observed to attach on the rough surface of GaN nanowires (Figure 1 b). The different morphology implies that P doping has a strong influence on the structure of the GaN nanowires. Typically the nanowires with P doping have average diameters of ∼100 nm and lengths of up to tens of micrometers as shown in Figure 1a. The representative Y-shaped GaN junction with a diameter

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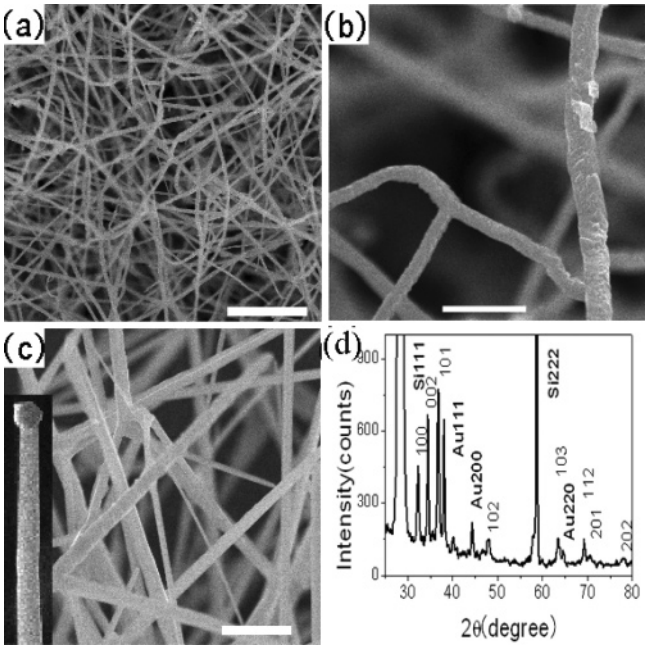

Figure 1. Low-magnification (a) and high-magnification (b) SEM image for P-doped GaN nanowires. (c) Typical SEM image for GaN nanowires without P doping (inset: representative individual pure GaN nanowire). (d) XRD pattern for the as-synthesized GaN nanowires with P doping. Scale bars in a−c are 5 μm, 300 nm, and 1 μm, respectively.

of ca. 100 nm shown in Figure 1b indicates that P doping could also lead to the curving and branches of the nanowires.

XRD measurement for the P-doped GaN nanowires is shown in Figure 1d, revealing that the as-synthesized nanowires are wurtzite-type hexagonal GaN with lattice constants of $a = 0.318$ nm and $c = 0.518$ nm. The signals from Si substrate and Au catalyst could also be detected.

Details on the structure and crystallinity of GaN nanowires are further obtained with TEM analysis. Figure 2a shows the low-magnification TEM image for the P-doped GaN nanowires after ultrasonic dispersion in alcohol solution during TEM sample preparation. The long silk-like GaN nanowires observed in the SEM images have been broken into short rodlike nanorods by ultrasonic operation, implying the poor quality of the GaN nanowires with P doping. A typical nanowire with particles attaching on the surface (Figure 2b) reveals that the rough surface of GaN nanowires easily absorbs nanosized particles. The herringbone-like rough surface of P-doped GaN nanowires is further illustrated in Figure 2c. Sawtooth-like edges protruding from the nanowire surface could be clearly observed. Careful TEM observation indicates that the nanowires are composed of two layers of sheets with screwing and twisting growth along the wire axis, as shown in Figure 2d. The two sheets in an individual nanowire could also be confirmed in Figure 2a, in which the contrast of the central axis of nanowires seems brighter compared to the two sides, indicating a different thickness in the center and edges. The Au particle attached on the tip of GaN nanowires indicates that a vapor−liquid−solid (V−L−S) growth mechanism is responsible for nanowire formation.[14,15] Chemical composition analysis performed on an individual GaN nanowire confirms that the nanowire is mainly composed of Ga and N, and the P element signal can also be easily detected as depicted in Figure 2e. Further analysis by nano-electron-beam techniques indicates that the area around the axis of the nanowire has a relatively high content of P distribution compared with the edges. The P content in GaN nanowires is estimated to be from 3 to 5 at. %, as determined

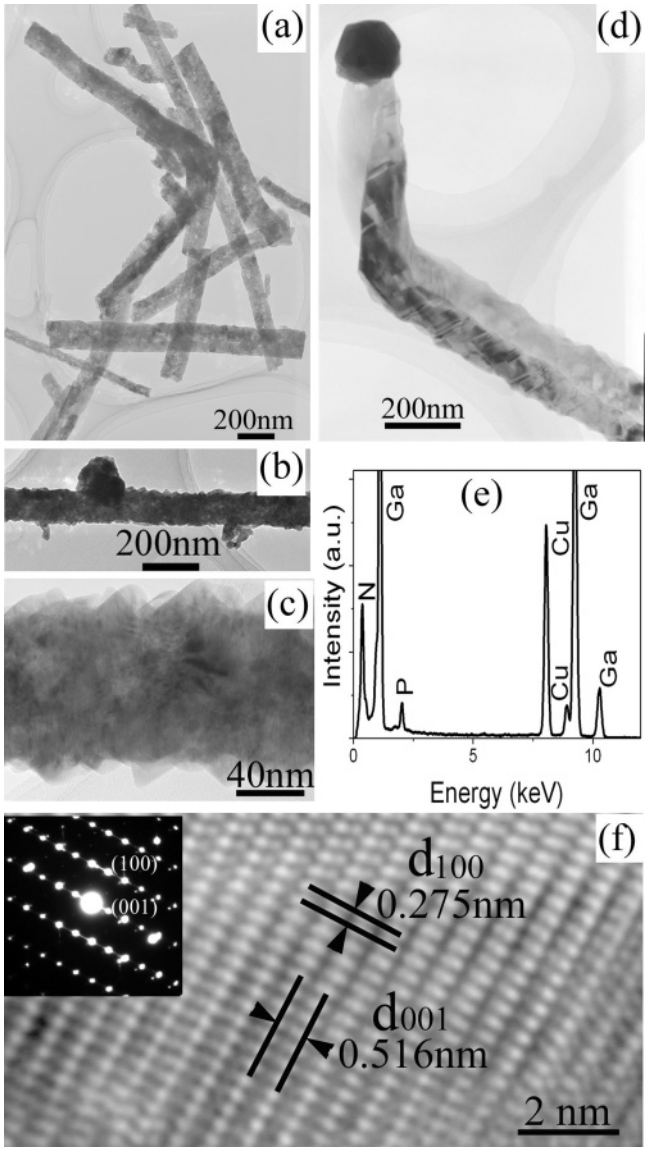

Figure 2. (a) Low-magnification TEM image for P-doped GaN nanowires after ultrasonic dispersion. (b) Typical TEM image for nanowires with nanoparticles on the surface. (c) TEM image for P-doped GaN nanowires with herringbone-like morphology. (d) Low-magnification TEM image for P-doped GaN nanowires with Au particle attached on the tip. (e) EDS spectrum recorded on single P-doped GaN nanowires. (f) High-resolution TEM image for the edge of P-doped GaN nanowires (inset: ED pattern taken along the [010] zone axis.).

from tens of P-doped GaN nanowires. The high-resolution TEM image and the corresponding electron diffraction (ED) pattern shown in Figure 2f reveal the single-crystalline characteristic of the P-doped GaN nanowires. The lattice fringes of the (001) and (100) planes are clearly seen with d spacings of ∼0.52 and 0.28 nm, respectively. The ED pattern can be indexed as the [010] zone axis of a wurtzite GaN crystal. Some extra minor diffraction spots could also be clearly observed from the shown ED pattern, which possibly result from the nanoparticles attaching on the nanowire surface (Figure 2b). Both the high-resolution TEM image and ED pattern confirm the crystalline characteristic for P-doping GaN nanowires.

Further evidence for P doping in GaN nanowires was confirmed by elemental maps for the ingredient elements. Details for the elemental map measurement can be found in our previous work.[16] Figure 3a shows a TEM image for P-doped GaN nanowire, and N and Ga could be clearly observed in the elemental maps as depicted in Figure 3b and c. Furthermore,

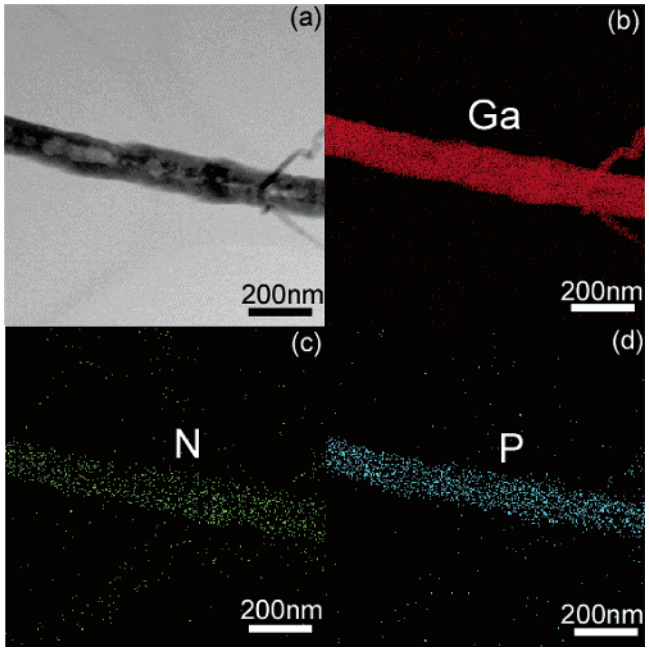

Figure 3. (a) TEM image of GaN nanowire and the corresponding elemental maps for (b) Ga, (c) N, and (d) P.

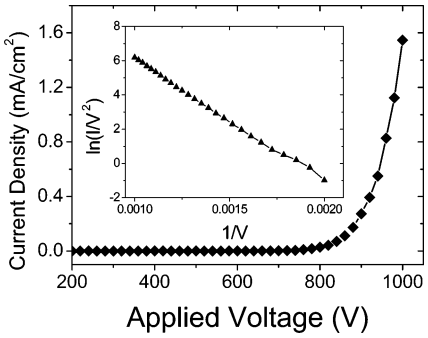

Figure 4. Field-emission $J-V$ curve measured at 150 μm separation between Cu-probe and P-doped GaN film (inset: corresponding F−N plot).

the P element could also be easily detected in the nanowire (Figure 3d), indicating that the P atoms have completely penetrated into the GaN nanowires during the process of nanowire formation.

With a direct band gap of 3.4 eV at room temperature, GaN is considered to be a good candidate for flat panel display application and blue light-emitting diodes (BLEDs) or other electronic and photonic devices.[17] The electron emission behavior for P-doped GaN nanowires was finally examined. The P-doped GaN nanowires film deposited on Si substrate is placed into the vacuum chamber in advance. A rodlike Cu probe with cross-sectional area 1 mm^2 is employed as the anode to induce the electrons from the cathode GaN film. Details for the field-emission device can be found in our previous reports.[18] After the vacuum reaches $\sim 2 \times 10^{-6}$ Torr, a dc voltage sweeping from 0 to 1000 V is applied along the Cu probe to the GaN film in selective separations between the anode and cathode until the short-cut current is detected. The effective emission area (A) for evaluating the current density and hoping field is approximately calculated[19] by $A = 2\pi RZ(2^{1/n} - 1)$, where $n = (d \ln I)/(d \ln V)$. Figure 4 shows a representative curve for emission current versus applied field ($J-E$) of the GaN film measured at a separation of 150 μm between the Cu probe and $GaN_{1-x}P_x$ film. Compared to the previous FE results for undoped GaN nanowires,[19] we adopted the same definition for the turn-on field, an electric field to produce a current of 0.01 mA/cm^2. The turn-on field obtained from the $J-E$ curve shown in Figure 4 is estimated to 5.1 V/μm, lower than the previously reported turn-on fields of ~6.1 or 12 V/μm for undoped GaN nanowires and that of ~6.4 V/μm for polycrystalline bulk GaN.[20−22] Compared to the undoped GaN nanowires reported previously,[19] the P-doped GaN nanowires have larger diameters. Our intensive experiments also indicated that there is little difference in the film thickness and density for the doped/undoped GaN films. Therefore, it is believed that the lower value of the turn-on electric field for current GaN nanowires mainly came from the rough surface (Figure 1b), which resulted from P doping. The rough surface with a large amount of nano-needlelike facets ensures that the GaN nanowires possess a high geometry enhancement factor, which will reduce the anode voltage needed for electron emission from the surface of GaN film. Similar phenomena have also been reported for GaN nanobelts with herringbone-like morphology, MoS_2 nanoflowers, and ZnO nanoneedles.[20,23−24] The inset of Figure 4 displays the corresponding Fowler−Nordheim (F−N) plots for the $J-E$ curve. The linearity of the F−N curve indicates that electron emission for the P-doped GaN nanowires possibly results from a quantum mechanical tunneling process, as reported in ref 18.

Conclusion

Uniform and well-crystallized GaN nanowires with P doping were synthesized via a simple chemical vapor deposition process. GaN nanowires with P doping have a rough surface and a turn-on field as low as 5.1 V/μm at room temperature. The excellent field-emission characteristic indicates that P-doped GaN nanowires are good candidates as electron emitters and hold promise for flat panel display application in future nanodevice design. Furthermore, it would be interesting to explore the incorporation of other dopants into various nanostructured semiconductors.

References and Notes

(1) Wu, J.; Walukiewicz, W.; Yu, K. M.; Ager, J. W., III; Haller, E. E.; Hong, Y. G.; Xin, H. P.; Tu, C. W. *Phys. Rev. B* **2002**, *65*, 241303.
(2) Weyers, M.; Sato, M. *Appl. Phys. Lett.* **1993**, *62*, 1396.
(3) Sánchez-Páramo, J.; Calleja, J. M.; Sánchez-García, M. A.; Calleja, E. *Appl. Phys. Lett.* **2001**, *78*, 4124.
(4) Monroy, E.; Andreev, T.; Holliger, P.; Bellet-Amalric, E.; Shibata, T.; Tanaka, M.; Daudin, B. *Appl. Phys. Lett.* **2004**, *84*, 2554.
(5) Lee, J. H.; Hahm, S. H.; Lee, J. H.; Bae, S. B.; Lee, K. S.; Cho, Y. H.; Lee, J. L. *Appl. Phys. Lett.* **2003**, *83*, 917.
(6) Sasaki, T.; Sonoda, S.; Yamamoto, Y.; Suga, K.; Shimizu, S.; Kindo, K.; Hori, H. *J. Appl. Phys.* **2002**, *91*, 7911.
(7) Iwata, K.; Asahi, H.; Asami, K.; Gonda, S. *J. Cryst. Growth* **1997**, *175/176*, 150.
(8) Liu, X.; Bishop, S. G.; Baillargeon, J. N.; Cheng, K. Y. *Appl. Phys. Lett.* **1993**, *63*, 208.
(9) Cheng, G. S.; Zhang, L. D.; Zhu, Y.; Fei, G. T.; Li, L.; Mo, C. M.; Mao, Y. Q. *Appl. Phys. Lett.* **1999**, *75*, 2455.
(10) Jiang, K.; Chen, X. L.; He, M.; Wang, W. J.; Zhang, X. N.; Shen, F. *Chem. Phys. Lett.* **2003**, *368*, 416.
(11) Hu, J. Q.; Bando, Y.; Golberg, D.; Liu, Q. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3493.
(12) Nakamura, S.; Pearton, S. J.; Fasol, G. *The Blue Laser Diode: The Complete Story*; Springer: Berlin, 2000.
(13) Tang, C. C.; Fan, S. S.; Dang, H. Y.; Li, P.; Liu, Y. M. *Appl. Phys. Lett.* **2000**, *77*, 1961.
(14) Wagner, R. S.; Eliis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
(15) Duan, X. F.; Lieber, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 188.
(16) Golberg, D.; Changzhi Gu, C. Z.; Bando, Y.; Mitome, M.; Tang, C. C. *Acta Mater.* **2005**, *53*, 1583.
(17) Zhong, Z.; Qian, F.; Wang, D.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 343.
(18) Tang, C. C.; Bando, Y. *Appl. Phys. Lett.* 2**003**, *83*, 659.
(19) Zhu, W.; Bower, C.; Kochanski, G. P.; Jin, S. *Solid-State Electron.* **2001**, *45*, 921.

(20) Luo, L.; Yu, K.; Zhu, Z.; Zhang, Y.; Ma, H.; Xue, C.; Yang, Y.; Chen, S. *Mater. Lett.* **2004**, *58*, 2893.
(21) 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.
(22) Yamanaka, T.; Tampo, H.; Yamada, K.; Ohnishi, K.; Hashimoto, M.; Asahi, H. *Phys. Stat. Sol (c)* **2002**, *1*, 469.
(23) Li, Y. B.; Bando, Y.; Golberg, D. *Appl. Phys. Lett.* **2003**, *82*, 1962.
(24) Li, Y. B.; Bando, Y.; Golberg, D. *Appl. Phys. Lett.* **2004**, *84*, 3603.