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Structure and photoluminescence of wurtzite/zinc-blende heterostructure GaN nanorods

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GaN nanorods with a wurtzite/zinc-blende (WZ/ZB) heterostructure are synthesized by chemical vapor deposition. They have a triangular cross section and grow along the WZ $[01\bar{1}0]$ direction. The WZ and ZB phases appear alternately along the nanorod's transverse direction, forming a type-II superlattice structure. Two ultraviolet emission peaks dominate the photoluminescence spectra of the GaN nanorods. One originates from excitonic transitions within the WZ regions. The other shows an anomalous "S-shaped" energy shift with increasing temperature, and is attributed to radiative recombinations of carriers localized at potential fluctuations in ZB regions. The carrier localization also results in high luminescent efficiency of the GaN nanorods. © 2009 American Institute of Physics. [doi:10.1063/1.3240890]

As building blocks for future nanodevices and an ideal platform for the fundamental physical research in nanoscale, one-dimensional (1D) semiconductor nanostructures have currently become a focus of intense research. Gallium nitride (GaN) is an attractive material for developing blue-ultraviolet optoelectronic devices and high-power, high-temperature, high-speed electronic devices because of its wide band gap, strong chemical bonding, and high saturation electron drift velocity. In recent years, great efforts have been made to investigate 1D GaN nanostructures. GaN nanowires and nanotubes have been synthesized by various techniques, such as template-confined growth,¹⁻³ arc discharge,⁴ laser ablation,⁵ chemical vapor deposition (CVD),⁶⁻¹³ molecular beam epitaxy, etc.¹⁴ High-performance 1D GaN nanodevices, including light-emitting diodes,¹⁵ field effect transistors,^{16,17} field emission devices,⁸ and logic gates,¹⁷ have also been demonstrated.

It is known that GaN can exist in both stable wurtzite (WZ) structure and metastable zinc-blende (ZB) structure. At room temperature, their band gaps are 3.4 and 3.2 eV, respectively. Compared to the more common WZ phase, the ZB phase, with higher crystallographic symmetry, offers certain advantages, including higher carrier mobility and easier *p*-type doping.¹⁸ More importantly, based on their different energy band structures, WZ and ZB GaN can be utilized to construct a unique quantum well structure, where both barrier and well have the same chemical composition. Theoretical work has predicted that the optical gain in ZB GaN quantum wells might be higher than that in WZ GaN wells.¹⁸ However, as reported in many literatures, most GaN nanowires crystallize in the stable WZ structure,^{1-11,13,14} only a few groups have observed the embedded ZB phase in WZ GaN nanowires.^{8,19,20} In this work, we have synthesized GaN nanorods (NRs) with an alternating WZ/ZB heterostructure by a CVD method. Their photoluminescence (PL) properties were studied and found to be closely related to their unique structural feature.

The synthesis of GaN NRs was carried out in a horizontal quartz tube furnace. A mixture of 0.15 g Ga and 0.4 g

Ga_2O_3 , serving as the starting material, was placed at the center of the CVD furnace. Si substrates were put at the downstream side to collect the products. The quartz tube was evacuated and then purged with high purity Ar. When the furnace was heated to 800 °C, the Ar flow was replaced by ultrapure NH_3 , which acted as a reactive gas. The furnace temperature continued to increase to 1000 °C, and was kept there for about 2 h. The reaction pressure was controlled within 20–40 mbar. Finally, the furnace was naturally cooled down to room temperature, while the sample was still under the NH_3 flow. The morphology, structure and composition of the products were characterized by scanning electron microscopy (SEM) (FEI Quanta 400F), high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai 20) and energy dispersive x-ray (EDX) spectroscopy. The samples were mounted on a cold finger in a closed-cycle He cryostat for temperature-dependent PL measurements. The 325 nm line of a He–Cd laser was employed as the excitation source.

Figure 1 displays representative SEM images of the

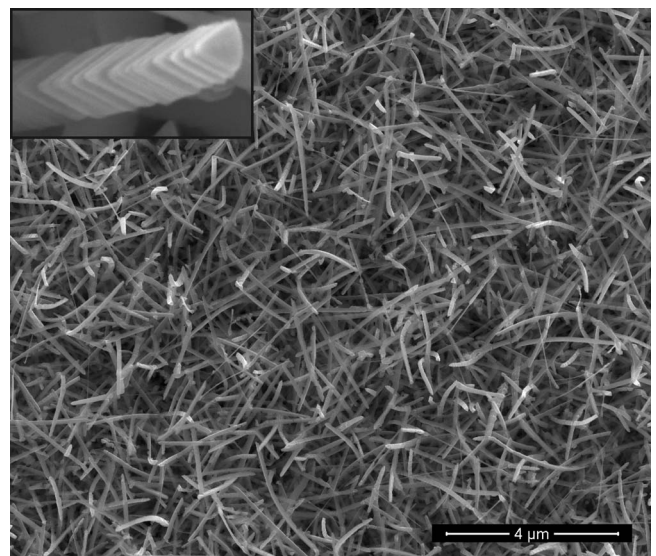


FIG. 1. Typical SEM image of the synthesized GaN NRs. A high magnification SEM image in the inset clearly shows that the NR has a triangular cross section.

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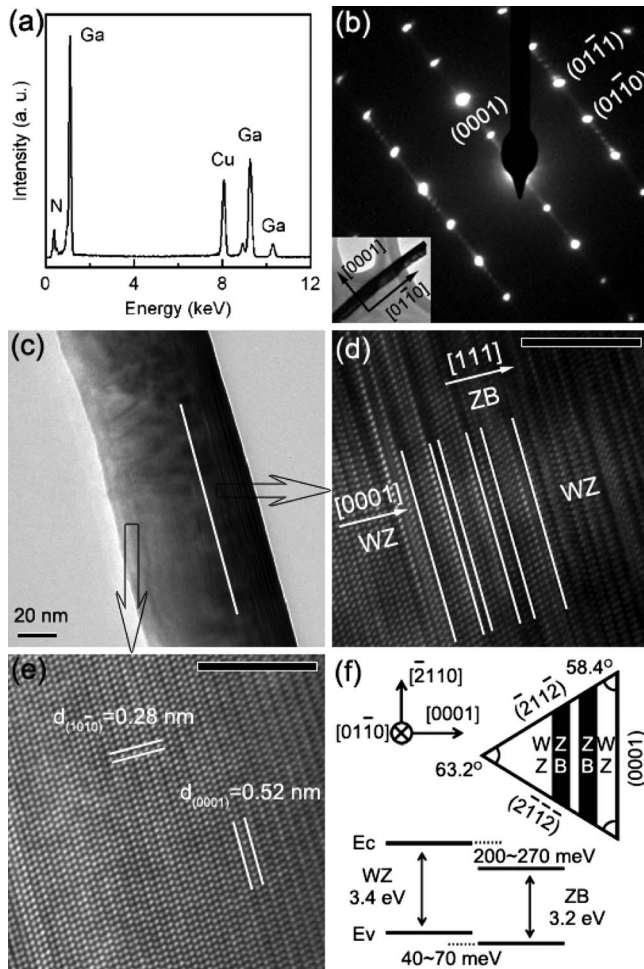


FIG. 2. (a) EDX spectrum of an individual GaN NR. (b) SAED pattern of a single GaN NR obtained along the WZ $[2\bar{1}\bar{1}0]$ zone axis. Inset indicates the direction of the corresponding NR. (c) TEM image of a single GaN NR. (d) and (e) are the HRTEM images of right and left regions of GaN NR in (c), respectively. Scale bars are 5 nm. (f) Schematic diagram of a $[01\bar{1}0]$ -axis NR and the energy band diagram of WZ/ZB GaN heterojunction.

product. It can be seen that a high density of NRs uniformly covers the entire Si substrate. The NRs have a narrow size distribution, with an average diameter of ~ 100 nm and lengths of several micrometers. A closer look reveals that they have a triangular cross section, and two of three side surfaces are corrugated. The EDX spectrum in Fig. 2(a) illustrates that the synthesized product consists of only Ga and N. The Cu signal comes from the TEM grid. Quantitative analyses determine the average atomic ratio of Ga/N as 56:44, indicating the formation of slightly Ga-rich GaN NRs.

Figure 2(b) is a selected area electron diffraction (SAED) pattern taken from a single GaN NR, which can be indexed to the $[2\bar{1}\bar{1}0]$ zone axis of the WZ structure. SAED studies on many NRs confirm that they are crystalline, and grow along the $[01\bar{1}0]$ direction. SEM observations have also revealed that the cross section of GaN NRs is close to an isosceles triangle. These results imply that the NRs are enclosed by the (0001), $(\bar{2}11\bar{2})$ and $(2\bar{1}\bar{1}2)$ side planes, as depicted in Fig. 2(f), in agreement with published data.^{13,19} Kuykendall *et al.*¹³ had demonstrated the selective epitaxial growth of $[01\bar{1}0]$ -oriented, triangular GaN nanowire arrays on (100) γ -LiAlO₂ substrate. However, the random orientation of our NRs indicates an absence of similar epitaxial

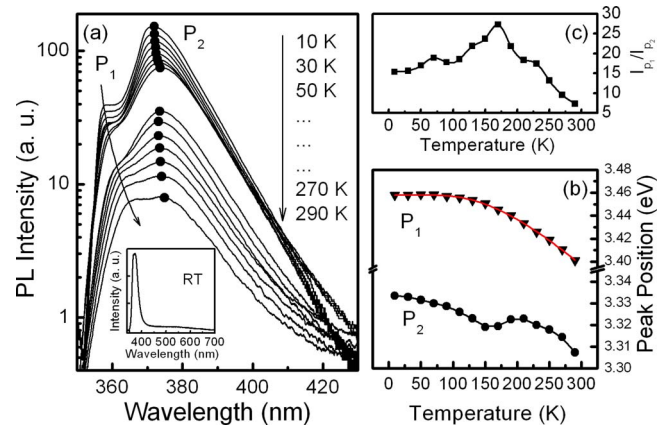


FIG. 3. (Color online) (a) UV PL spectra of GaN NRs at different temperatures from 10 to 290 K in 20 K increments. Its inset is a room-temperature PL spectrum in the wavelength range of 340–700 nm. (b) The temperature dependence of P_1 and P_2 peak energies; the red line is a fit to the data points (triangles) following a Bose–Einstein expression. (c) The integrated intensity ratios of P_2 to P_1 peak as a function of temperature.

relationship. Several groups had also observed that the Ga/N reactant ratio in the vapor phase plays an important role in determining the morphology and growth direction of GaN nanostructures.^{21,22} Ga-rich environment is thought to result in low formation energy of {0001} polar surfaces and high diffusivity of adatoms on such planes, which favor the extension of {0001} surfaces. Therefore, the $[01\bar{1}0]$ orientation of our GaN NRs may be traced to a Ga-rich growth condition, which is also suggested by our EDX analyses.

It is worth noting that some darker satellite spots are equidistantly distributed between adjacent (0001) diffraction spots [Fig. 2(b)], and alternating light/dark stripes appear parallel to the transverse direction and on the right region of the NR [Fig. 2(c)]. Both facts suggest the presence of the quasi-periodic microstructures, which were further studied by HRTEM. Figure 2(e) shows lattice resolved TEM image of the left region of the NR in Fig. 2(c). The near-perfect lattice fringes, with interplanar spacings of 0.52 and 0.28 nm, correspond to the orthogonal (0001) and $(10\bar{1}0)$ planes of WZ GaN. Few dislocations or stacking faults were observed in this region. However, in its right region, both WZ (hexagonal) and ZB (cubic) phases of GaN appear alternately along the NR's transverse direction, as shown in Fig. 2(d). The phase transition is achieved by stacking faults of the cubic (111) and hexagonal (0001) planes, due to small formation energy difference between two crystalline phases (~ 10 meV/atom).²³ A similar heterostructure has also been observed in ZnS and InAs nanowires. The formation of such a structure is thought to result from slight fluctuations in growth parameters, or from strain accumulation and relaxation during growth.^{24–26}

It is generally accepted that WZ/ZB GaN may form a type-II band alignment, with conduction and valence band offsets of 220–270 and 40–70 meV,^{23,27–29} respectively, as shown in Fig. 2(f). Thus, the novel optical properties are expected for these NRs. Figure 3(a) shows their PL spectra measured at different temperatures from 10 to 290 K. A strong ultraviolet (UV) near-band-edge emission, as well as a relatively weak yellow deep-level emission associated with structural defects or impurities, appears in the room temperature spectrum. It is noted that the UV emission band consists

of two peaks. At 10 K, they center at 358 nm (3.46 eV, P_1) and 372 nm (3.33 eV, P_2), respectively. The P_1 peak corresponds to free and/or bound exciton transitions in WZ GaN. As the temperature increases, its intensity gradually decreases, due to the thermal dissociation of excitons; and its peak position shifts to lower energy. Figure 3(b) shows the temperature dependence of the P_1 peak energy, which can be well fitted by a Bose–Einstein expression: $E(T) = E(0) - \lambda / [\exp(\beta/T) - 1]$, with the parameters $E(0) = 3.46$ eV, $\lambda = 35.1$ meV, and $\beta = 572$ K. This indicates that the electron-phonon interaction dominates the redshift of the P_1 peak in the measured temperature range.

For the P_2 peak at 3.33 eV, there are few reports available. In fact, the very thin ZB layers embedded in the WZ matrix may be regarded as stacking faults, and vice versa. The electrons can be confined in ZB layers, which attract holes via Coulomb interactions to form excitons.²⁷ Paskov *et al.* had observed an emission at around 3.4 eV, and attributed it to excitons bound to stacking faults.²⁸ Lu *et al.*²⁹ had demonstrated that the stacking fault emission behaves like a spatially indirect transition between WZ and ZB GaN, which leads to an emission at 3.17 eV. However, these emissions are absent in our WZ/ZB GaN NRs. A donor-acceptor pair (DAP) emission is usually observed at 3.28 eV in low-temperature PL spectra of WZ GaN. However, the study on excitation power-dependent PL spectra (not shown here) does not support DAP as the origin of the P_2 peak. On the other hand, ZB GaN usually shows near-band-edge emissions at 3.27–3.30 eV at low temperatures,³⁰ which is close in energy to the P_2 peak. The small relative blueshift is due to carrier confinement effect in several atomic-layer thick ZB layers. Thus, the P_2 peak may be associated with the band to band transitions in ZB GaN layers. Similar assignments of P_1 and P_2 like peaks have also been reported in GaN nanowires.^{8,20} It is interesting to note in Fig. 3(b) that the P_2 peak position exhibits a so-called “S-shaped” temperature dependence, i.e., a red-blue-redshift with increasing temperature. The S-shaped behavior, as well as the asymmetrical lineshape of P_2 peak, is a typical indication of carrier localization at potential fluctuations.^{31,32} For our GaN NRs, the potential fluctuations are likely to be caused by structural disorder, such as rough WZ/ZB interface, nonuniform ZB layer thickness and point defects in the ZB layers. The slight blueshift of P_2 peak, appearing in the middle temperature range of 150–210 K, is due to thermal delocalization of carriers from the potential fluctuations. The following redshift is dominated by the ordinary temperature-induced band gap shrinkage. Moreover, the intensity of P_2 peak is found to decay abruptly when the temperature increases from 150 to 170 K. Figure 3(c) gives the integrated intensity ratios of the P_2 to P_1 peak at different temperatures, which increase up to 170 K, and then decrease rapidly. These observations indicate that the carrier localization can lead to higher luminescence efficiency.

In summary, we have synthesized an interesting type of GaN NRs with alternating WZ/ZB heterostructures, and studied their microstructure-related PL properties. Two UV emission peaks from the WZ and ZB layers, respectively, are found in the PL spectra of GaN NRs. The S-shaped PL behavior is understood in terms of a carrier localization model. Such 1D GaN superlattice nanostructures have potential applications in future optoelectronic nanodevices.

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- ¹W. Q. Han, S. S. Fan, Q. Q. Li, and Y. D. Hu, *Science* **277**, 1287 (1997).
- ²J. Goldberger, R. He, Y. Zhang, S. Lee, H. Yan, H. J. Choi, and P. Yang, *Nature (London)* **422**, 599 (2003).
- ³G. S. Cheng, L. D. Zhang, Y. Zhu, G. T. Fei, L. Li, C. M. Mo, and Y. Q. Mao, *Appl. Phys. Lett.* **75**, 2455 (1999).
- ⁴W. Han, P. Redlich, F. Ernst, and M. Rühle, *Appl. Phys. Lett.* **76**, 652 (2000).
- ⁵X. F. Duan and C. M. Lieber, *J. Am. Chem. Soc.* **122**, 188 (2000).
- ⁶X. Chen, J. Li, Y. Cao, Y. Lan, H. Li, M. He, C. Wang, Z. Zhang, and Z. Qiao, *Adv. Mater.* **12**, 1432 (2000).
- ⁷M. He, I. Minus, P. Zhou, S. N. Mohammed, J. B. Halpern, R. Jacobs, W. L. Sarney, L. Salamanca-Riba, and R. D. Vispute, *Appl. Phys. Lett.* **77**, 3731 (2000).
- ⁸C. C. Chen, C. C. Yeh, C. H. Chen, M. Y. Yu, H. L. Liu, J. J. Wu, K. H. Chen, L. C. Chen, J. Y. Peng, and Y. F. Chen, *J. Am. Chem. Soc.* **123**, 2791 (2001).
- ⁹X. Chen, J. Xu, R. M. Wang, and D. Yu, *Adv. Mater.* **15**, 419 (2003).
- ¹⁰S. Y. Bae, H. W. Seo, J. Park, H. Yang, H. Kim, and S. Kim, *Appl. Phys. Lett.* **82**, 4564 (2003).
- ¹¹J. Liu, X. M. Meng, Y. Jiang, C. S. Lee, I. Bello, and S. T. Lee, *Appl. Phys. Lett.* **83**, 4241 (2003).
- ¹²J. Q. Hu, Y. Bando, J. H. Zhan, F. F. Xu, T. Sekiguchi, and D. Golberg, *Adv. Mater.* **16**, 1465 (2004).
- ¹³T. Kuykendall, P. J. Pauzauskie, Y. Zhang, J. Goldberger, D. Sirbully, J. Denlinger, and P. Yang, *Nature Mater.* **3**, 524 (2004).
- ¹⁴R. K. Debnath, R. Meijers, T. Richter, T. Stoica, R. Calarco, and H. Lüth, *Appl. Phys. Lett.* **90**, 123117 (2007).
- ¹⁵H. M. Kim, T. W. Kang, and K. S. Chung, *Adv. Mater.* **15**, 567 (2003).
- ¹⁶A. Motayed, M. Vaudin, A. V. Davydov, J. Melngailis, M. He, and S. N. Mohammad, *Appl. Phys. Lett.* **90**, 043104 (2007).
- ¹⁷Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K. H. Kim, and C. M. Lieber, *Science* **294**, 1313 (2001).
- ¹⁸S. Dhara, A. Datta, C. T. Wu, Z. H. Lan, K. H. Chen, Y. L. Wang, C. W. Hsu, C. H. Shen, L. C. Chen, and C. C. Chen, *Appl. Phys. Lett.* **84**, 5473 (2004).
- ¹⁹D. Tham, C. Y. Nam, and J. E. Fischer, *Adv. Funct. Mater.* **16**, 1197 (2006).
- ²⁰B. W. Jacobs, V. M. Ayres, M. P. Petkov, J. B. Halpern, M. He, A. D. Baczewski, K. McElroy, M. A. Crimp, J. Zhang, and H. C. Shaw, *Nano Lett.* **7**, 1435 (2007).
- ²¹C. Y. Nam, D. Tham, and J. E. Fischer, *Appl. Phys. Lett.* **85**, 5676 (2004).
- ²²X. M. Cai, A. B. Djurišić, M. H. Xie, C. S. Chiu, and S. Gwo, *Appl. Phys. Lett.* **87**, 183103 (2005).
- ²³Z. Z. Bandić, T. C. McGill, and Z. Ikonik, *Phys. Rev. B* **56**, 3564 (1997).
- ²⁴P. Caroff, K. A. Dick, J. Johansson, M. E. Messing, K. Deppert, and L. Samuelson, *Nat. Nanotechnol.* **4**, 50 (2009).
- ²⁵J. Yan, X. Fang, L. Zhang, Y. Bando, U. K. Gautam, B. Dierre, T. Sekiguchi, and D. Golberg, *Nano Lett.* **8**, 2794 (2008).
- ²⁶J. S. Jie, W. J. Zhang, Y. Jiang, X. M. Meng, J. A. Zapien, M. W. Shao, and S. T. Lee, *Nanotechnology* **17**, 2913 (2006).
- ²⁷Y. T. Rebane, Y. G. Shreter, and M. Albrecht, *Phys. Status Solidi A* **164**, 141 (1997).
- ²⁸P. P. Paskov, R. Schifano, B. Monemar, T. Paskova, S. Figge, and D. Hommel, *J. Appl. Phys.* **98**, 093519 (2005).
- ²⁹X. H. Lu, P. Y. Yu, L. X. Zheng, S. J. Xu, M. H. Xie, and S. Y. Tong, *Appl. Phys. Lett.* **82**, 1033 (2003).
- ³⁰I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, *J. Appl. Phys.* **89**, 5815 (2001).
- ³¹K. B. Lee, P. J. Parbrook, T. Wang, F. Ranalli, T. Martin, R. S. Balmer, and D. J. Wallis, *J. Appl. Phys.* **101**, 053513 (2007).
- ³²Y. H. Cho, G. H. Gainer, A. J. Fischer, J. J. Song, S. Keller, U. K. Mishra, and S. P. DenBaars, *Appl. Phys. Lett.* **73**, 1370 (1998).