Effect of the Coating on the Structure and Optical Properties of GaN Nanowires

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Structural and optical properties of as-synthesized, Ga_2O_3-coated, and Al_2O_3-coated GaN nanowires are examined in this paper. GaN nanowires were synthesized by thermal evaporation of ball-milled GaN powders in an NH_3 atmosphere. The thermal annealing of the as-synthesized GaN nanowires in an argon atmosphere allows their surfaces to be oxidized, leading to the formation of 2nm-thick Ga_2O_3 layers. For the oxidized GaN nanowires, the distances between the neighboring lattice planes are shortened, and an excitonic emission band is remarkably enhanced in intensity, compared with the as-synthesized GaN nanowires. In addition, the as-synthesized GaN nanowires were coated cylindrically with Al_2O_3 by atomic layer deposition technique. Our study suggests that the Al_2O_3-coating passivates some of surface states in the GaN nanowires.

Keywords : GaN nanowire, Thermal annealing, TEM

1. INTRODUCTION

Wide-bandgap GaN semiconductor nanowires (E_g = 3.4 eV at room temperature) have attracted much attention for the fabrication of nanometer-sized high-power electronic and blue-light-emitting optoelectronic devices[1,2]. To realize the fabrication of the nanowire-based nanoelectronic devices, the protection of the nanowires from contamination and from oxidation is of crucial importance[3,4]. In particular, the cylindrical growth of wider-bandgap material with good quality on the surface of the nanowires may be required for GaN-nanowire-based optoelectronic devices with more enhanced emission efficiency[5]. Furthermore, the cylindrically conformal coating of gate material on the nanowires is of important usefulness in achieving the high efficient performance of future nanoelectronic devices.

Two coating methods have been employed in this study to GaN nanowires. The first method is thermal oxidation, which is one of the most useful methods for oxide growth not only as an insulating gate material in conventional electronic devices but also as a cladding material in conventional optical devices. Oxides grown on semiconductors have lots of advantages including a lower interface state density and lower leakage current in electronic devices[6]. Ga_2O_3 formed after the oxidization of GaN thin films was characterized by the low refractive index and high static dielectric constant, and this oxide has also become a promising candidate for resolving the issues of surface passivation on GaN thin films[7]. Though the formation of the Ga_2O_3 layers on GaN thin films by using thermal treatment at oxygen ambient is well known, it has never been reported to form highly uniform Ga_2O_3 layers on GaN nanowires since the discovery of these nanowires[8-10]. The second method is the deposition of aluminum oxide (Al_2O_3) layers on GaN nanowires by atomic-layer deposition (ALD) technique. Al_2O_3 has been widely applied as corrosion resistant coating films[11]. And this oxide material has been also utilized as capacitor dielectrics and gate oxides in memory devices due to its high dielectric constant, very low permeability, and high thermal conductivity[12]. Especially, precise control in the thickness of Al_2O_3 films by ALD has been focused in the field of ultra thin memory devices [13,14]. Moreover, step coverage of Al_2O_3 films on patterned substrates has been recently investigated by ALD to develop conformality on films[14,15].

In this study, GaN nanowires were first grown on a Si (100) substrate from ball-milled GaN powders by thermal evaporation procedure, Ga_2O_3 layers were formed on the synthesized GaN nanowires through thermal oxidation, and Al_2O_3 layers were deposited on the nanowires by ALD. The structural and optical properties of the as-synthesized, Ga_2O_3-coated, and

Al_2O_3-coated GaN nanowires were then examined in this study by x-ray diffraction (XRD), scanning electron microscopy (SEM), selected area electron diffraction (SAED), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and photoluminescence (PL). Finally, our PL results are analyzed on the basis of energy diagrams.

2. EXPERIMENTAL PROCEDURE

A Si (100) substrate (10 mm×10 mm) coated with Ni catalyst nanoparticles was used for the growth of GaN nanowires. A nickel nitrate/ethanol solution (0.01 M) was coated on the surface of the Si substrate using a spin coater with 1200 rpm. Starting GaN powders were ground for 20 hours in the mechanical ball mill system using a steel vial with stainless steel balls. The catalyzed Si substrate was put on the top of a quartz boat loaded with the ball-milled GaN powders. The thermal evaporation of the ball-milled GaN powders was performed at 1000 ℃ for 1 hour under an NH_3 flow at a rate of 30 standard cubic centimeters per minute (sccm) at a constant pressure of 0.5 atm. GaN nanowires were synthesized on the Si substrate after cooling down. For the oxidation of their surfaces, the synthesized GaN nanowires were transferred into a horizontal quartz tube furnace and annealed at 1000 ℃ for 30min in argon ambient (300 sccm). Al_2O_3 layers were deposited on the synthesized GaN nanowires at a temperature of 300 ℃ with ALD technique. Trimethylaluminum (TMA) and distilled water (H_2O) were utilized as the precursors for the Al_2O_3 deposition. The process pressure was 280 and 250 mTorr for the dosing of chemical precursors and the argon purging, respectively. The deposition was performed for 50 cycles; one cycle for the deposition of Al_2O_3 was composed of TMA dosing (2 sec), Ar purging (20 sec), H_2O dosing (2 sec) and Ar purging (20 sec).

The structural and optical properties of the GaN nanomaterials were characterized by XRD (RIGAKU, D/MAX-ⅡA with CuKα radiation), field emission scanning electron microscopy (FE-SEM) (HITACHI, S-4700), TEM (Philips, CM30), HRTEM (JEOL, JEM 2010), and energy dispersive X-ray spectroscopy (EDX), Line profile (Philips, TECNAI). PL was conducted at 300 K for the analysis of optical properties, with the 325-nm line from a He-Cd laser and a spectrometer (SPEX, 1000 M).

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of starting GaN powders, ball-milled GaN powders, and products synthesized from the ball-milled powders.

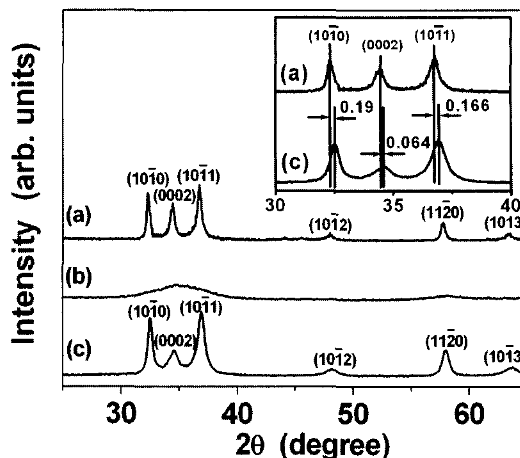

Fig. 1. XRD patterns of as-synthesized GaN nanowires (a), ball-milled GaN powders (b), and GaN powders (c).

The representative XRD pattern of the synthesized products is nearly identical to that of the starting powders, so their XRD pattern is accordingly indexed to the wurtzite structure of GaN. This indicates obviously that the products are identified to be GaN material.

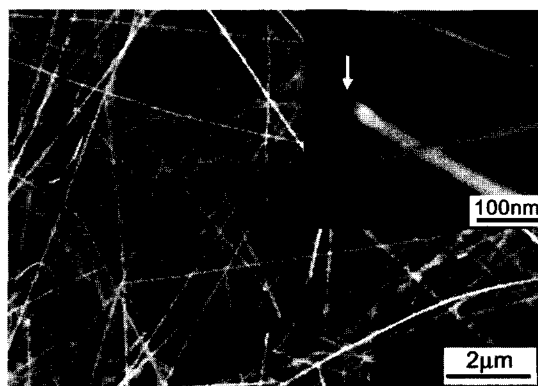

Fig. 2. SEM images of as-synthesized GaN nanowires. The inset exhibits that the GaN nanowire was terminated with a droplet at its tip.

Figure 2 shows SEM images of the GaN material. These SEM images demonstrate that the synthesized material is GaN nanowires with diameters of 20-70 nm, circular cross section, and lengths of about ten micrometers, and that one of the GaN nanowires was terminated with a droplet at its tip. A careful comparison between the XRD patterns of the as-synthesized GaN nanowires and the starting GaN powders (in the inset of Fig. 1) reveals that the XRD peaks for the nanowires are shifted to the lower Bragg angle, implying that distances between the neighboring lattice planes for the GaN powders are shortened than those for the as-synthesized GaN nanowires. The ball-milled GaN powders from which the GaN nanowires were synthesized are amor-

phous, as indicated in Fig. 1. The amorphousness of the GaN powders reduces the temperature of the thermal evaporation of these powders. GaN nanowires were not formed without the ball milling in our synthetic procedure; the ball milling helps the synthesis of other semiconductor nanowires as well[16,17]. In addition, it is worth noting that the GaN nanowires were not synthesized in any atmosphere of Ar, N_2, O_2, or air, but in an NH_3 atmosphere; it has been reported in our previous study that Ga_2O_3 nanobelts were synthesized in a N_2 or Ar atmosphere from the ball-milled GaN powders, and that Ga_2O_3 nanoparticles were formed in an O_2 atmosphere or in air[17,18].

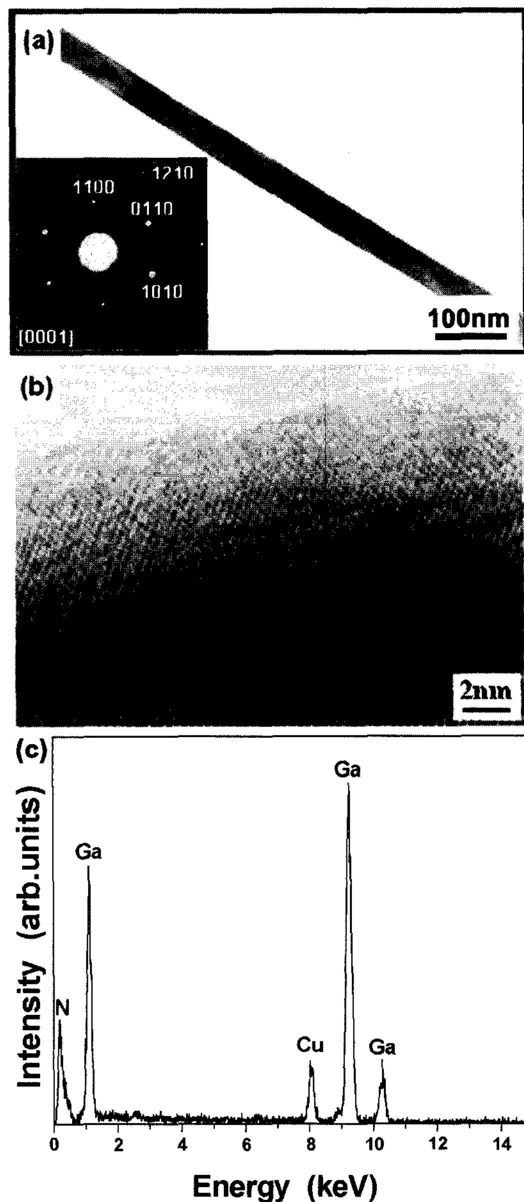

Fig. 3. TEM (a) and HRTEM (b) images of a selected GaN nanowire, and its associated EDX spectrum (c).

Figure 3 exhibits TEM and HRTEM images of a selected GaN nanowire, and its associated EDX spectrum. The TEM image of Fig. 3 (a) shows the straight-line morphology of the GaN nanowire with a diameter of about 65 nm. The SAED pattern in the inset of Fig. 3a demonstrates the single crystalline spots and the growth direction perpendicular to the $(10\bar{1}0)$ lattice plane. The HRTEM image of Fig. 3 (b) reveals the regular periodicity of lattice points in the synthesized GaN nanowire; any dislocation lines are not seen in this image. Notice that the amorphous layer with an atomic thickness is barely seen on the top surface of the nanowire. In the EDX spectrum depicted in Fig. 3 (c), only the peaks associated with Ga and N elements are present (the Cu-related peak in the spectrum come from the grids), leading to the obvious fact that the nanowires are indeed GaN material.

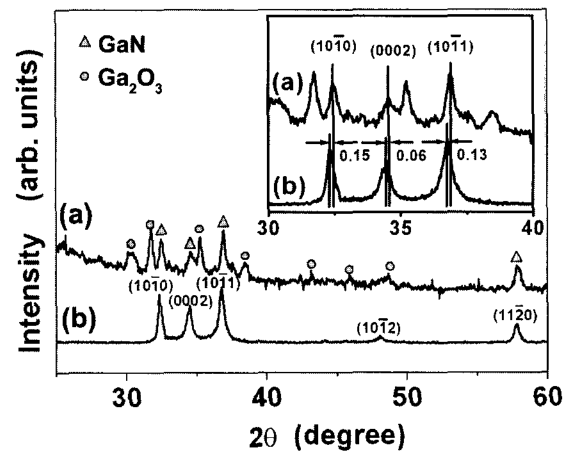

Fig. 4. XRD pattern of GaN nanowires annealed at 1000 ℃ in an Ar atmosphere (a) and the as-synthesized GaN nanowires (b).

Figure 4 shows an XRD pattern of GaN nanowires annealed at 1000 ℃ in an Ar atmosphere; for comparison, an XRD pattern of the as-synthesized GaN nanowires is given. Not only the GaN peaks but also the Ga_2O_3 peaks are present in the XRD pattern of the annealed GaN nanowires; the GaN and Ga_2O_3 peaks are marked by solid circles and solid triangles, respectively. A careful comparison between the XRD patterns in the inset of Fig. 4 reveals that the GaN-phased peaks for the annealed GaN nanowires are shifted to the higher diffraction angle, as compared with the as-synthesized GaN nanowires. The shift is $\Delta(2\theta) = 0.15$, 0.06, and 0.13 degrees for the $(10\bar{1}0)$, (0002), and $(10\bar{1}1)$ peaks, respectively. This shift indicates that the annealed GaN nanowires experience compressive stress due to the existence of the Ga_2O_3 in their surface.

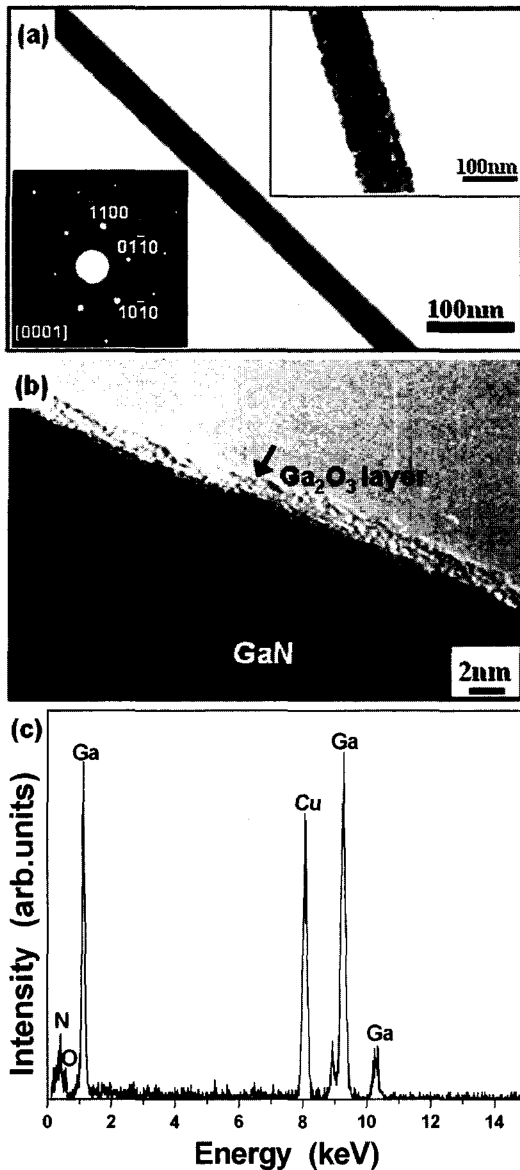

Fig. 5. TEM (a) and HRTEM (b) images of a selected GaN nanowire with oxidized surface, and its associated EDX spectrum (c).

Figure 5 exhibits TEM and HRTEM images of an annealed GaN nanowire, and its associated EDX spectrum. The TEM image and SAED pattern in Fig. 5 (a) still demonstrate the straight-line morphology of the annealed GaN nanowire and the single-crystalline spots, respectively. The HRTEM image of Fig. 5 (b) reveals the formation of a 2nm-thick layer on the surface of the GaN nanowire annealed in an Ar atmosphere; this layer is too thin to be seen in the TEM of Fig. 5 (a). The EDX spectrum of Fig. 5 (c) shows the presence of the O–related peak along with the Ga- and N- related peaks. The EDX spectrum and the XRD pattern(Fig. 4) suggest that the 2nm-thick layer formed in the surface of the annealed GaN nanowire be Ga_2O_3. In other words, the surface of the GaN nanowire is oxidized in an Ar atmosphere. A possible origin for the oxygen is the residual oxygen atoms in the supplied Ar gas [17,18]. Furthermore, the as-synthesized GaN nanowires were annealed at 1000 ℃ in an O_2 atmosphere. The TEM image of this annealed GaN nanowire in the inset of Fig. 5 (a) reveals the formation of Ga_2O_3 nanometer-sized grains in the surface of the annealed GaN nanowire. A comparison of the TEM images of the two annealed GaN nanowires shown in Fig. 5 (a) illustrates that the oxidized surface of the GaN nanowire annealed in an Ar atmosphere is much smoother. However, the surfaces of the GaN nanowires were not oxidized in an Ar or O_2 atmosphere at temperatures lower than 1000 ℃.

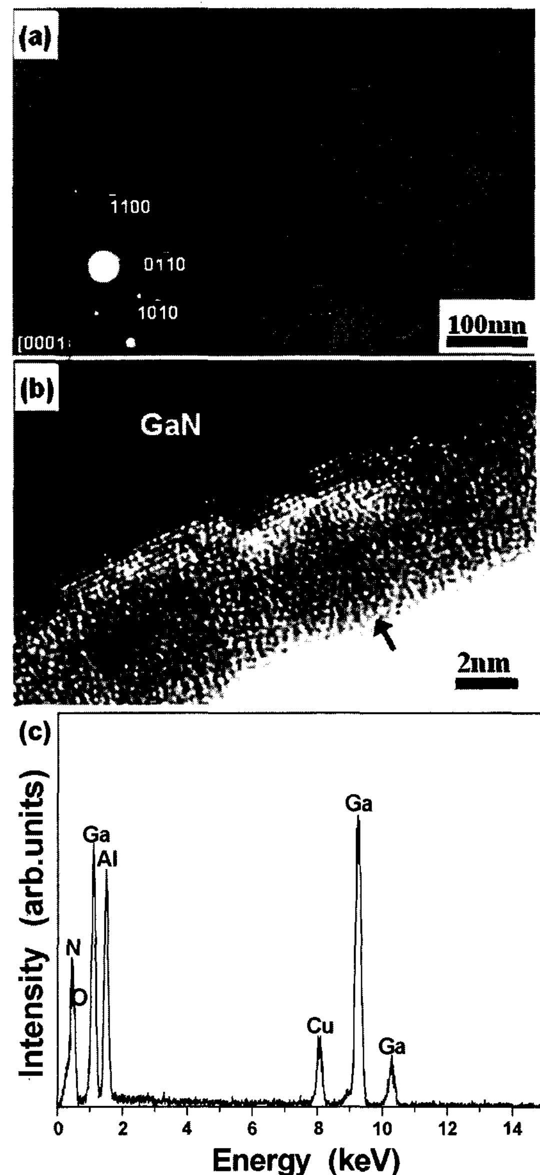

Fig. 6. TEM (a) and HRTEM (b) images of a selected Al_2O_3-coated GaN nanowire, and its associated EDX spectrum (c).

Figure 6 shows TEM and HRTEM images of a GaN nanowire coated with Al_2O_3 material by ALD, and its associated EDX spectrum. The TEM image of Fig. 6 (a) illustrates that the GaN nanowire is covered with an Al_2O_3 shell with a thickness of 10 nm. The halo in its SAED pattern comes from the amorphous Al_2O_3 layer. The HRTEM image of Fig. 6 (b) illustrates the periodic array of lattices in the core material of GaN and the randomly positioned lattices in the Al_2O_3 shell; it was observed that the Al_2O_3 material gets locally crystallized under the e-beam. The EDX spectrum of Fig. 6 (c) illustrates that the coated material is indeed Al_2O_3.

Figure 7 shows a TEM image, EDX line profiles, and illustration of an Al_2O_3-coated GaN nanowire; the line marked by 1 in the TEM image is the scanning way for the EDX line profiles. The TEM image of Fig. 7 (a) shows a GaN-core (white)/Al_2O_3-shell (dark) structure; the GaN core is about 50 nm in diameter and the Al_2O_3 shell is about 20 nm in thickness. Elemental concentration profiles of Al, O, Ga, and N across the Al_2O_3-coated GaN nanowire obtained from EDX spectra are drawn in Fig. 7 (b) (see the representative EDX spectrum of Fig. 6 (c); the resolution of the profiles is 2 nm, so the Al_2O_3-coated GaN nanowire with a shell thickness of 20 nm is utilized for this profile study.

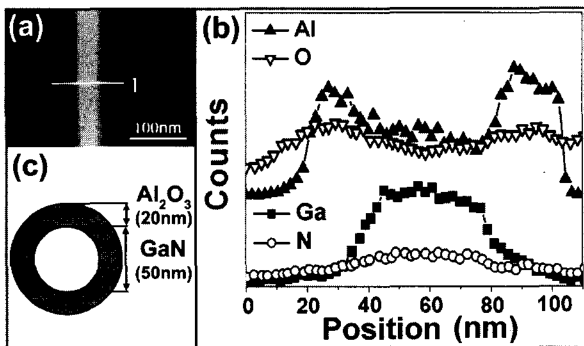

Fig. 7. TEM image (a), EDX line profiles (b), and illustration (c) of an Al_2O_3-coated nanowire.

The profiles of Al and O show the tubular geometry with concentration maxima on both sides and a central minimum, and the profiles of Ga and N are peaked in the center. These EDX line profiles may confirm that the Al_2O_3-coated GaN nanowire has indeed the GaN-core/Al_2O_3-shell structure. The illustration of Fig. 7 © describes the core/shell structure of the Al_2O_3-coated GaN nanowire on the basis of the TEM image and EDX line profiles. Note that the EDX line profiles could not be performed for the oxidized nanowires due to the too thin thickness of the oxide layer.

Figure 8 shows room-temperature PL spectra obtained for the as-synthesized, oxidized, and Al_2O_3-coated GaN nanowires. Some broad PL bands are present in the range of 2.4~3.6 eV in these PL spectra; nevertheless, the yellow band is absent in all three PL spectra. An interesting observation is that a PL band ranging from 3.1 to 3.6 eV is remarkably enhanced around hundred times in intensity when the surfaces of the GaN nanowires are oxidized. This PL band is strengthened in intensity, even when the surfaces of the GaN nanowires are coated with Al_2O_3. The enhanced PL band corresponds to the emission from the recombination of excitons; the lowering of the peak position and the broadening of the linewidth in the excitonic peaks observed for the GaN nanowires, compared with GaN epilayers, are caused by a variety of the stresses experienced by these nanowires[19].

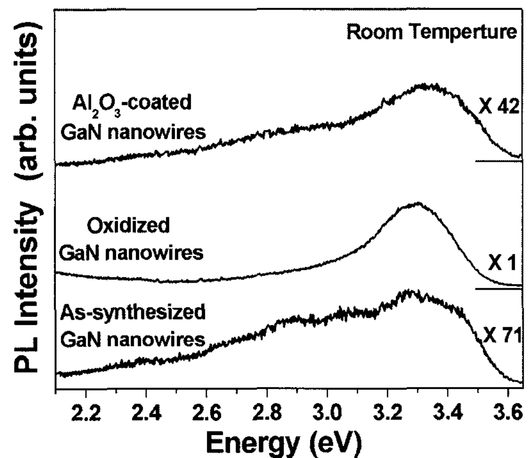

Fig. 8. PL spectra of as-synthesized GaN nanowires, GaN nanowires with oxidized surfaces, and Al_2O_3-coated GaN nanowires.

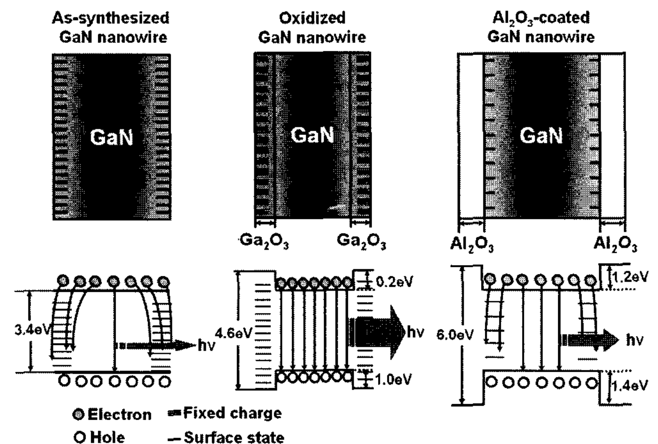

Fig. 9. Energy diagrams of as-synthesized GaN nanowires, GaN nanowires with oxidized surfaces, and Al_2O_3-coated nanowires, and illustration describing radiative and nonradiative recombination of excitons in these nanowires.

Energy diagrams are drawn in Fig. 9 for the as-synthesized GaN nanowires, the GaN nanowires with oxidized surface, and the Al_2O_3-coated GaN nanowires. The energy diagrams are constructed on the basis of the information provided by Refs. 20-21. The enhancement of the PL intensity in the excitonic emission band for the GaN nanowires with oxidized surface may be explained by the absence of the fixed charges at the Ga_2O_3/GaN interface.

In the as-synthesized GaN nanowires, surface states formed within the band gap may facilitate rapid nonradiative recombination of excitons photogenerated by the above-gap excitation; the surface states present in the surfaces of the as-synthesized GaN nanowires are caused by dangling bonds, defects, or impurities (dangling bonds act as getters for ambient impurities). Most photoexcited excitons wonder in the micrometer range before the recombination, reach the surfaces, and recombine nonradiatively through the surface states[22]. In contrast to the as-synthesized GaN nanowires, for the GaN nanowires with oxidized surface, the surface states are present within the Ga_2O_3 layer, and the potential barriers of the Ga_2O_3 layer do not allow the photoexcited excitons to reach the fixed charges. In this energy diagram, most photoexcited excitons recombine radiatively, emitting strong emission. In the case of the Al_2O_3-coated nanowires, although the surface states are present at the Al_2O_3/GaN interface, these nanowires still emit stronger excitonic emission, compared with the as-synthesized GaN nanowires. This observation indicates that the coating of Al_2O_3 passivates some of the surface states.

4. CONCLUSION

GaN nanowires with thicknesses in the range of 20 to 70 nm were synthesized by thermal evaporation of ball-milled GaN powders at 1000 ℃ in an NH_3 atmosphere, and the thermal annealing of the as-synthesized GaN nanowires in an argon atmosphere at 1000 ℃ forms an uniform Ga_2O_3 layer of a thickness of 2 nm in the their surfaces. The distances between the neighboring lattice planes for the annealed GaN nanowires are shortened due to the existence of the Ga_2O_3 in their surface, compared with the as-synthesized GaN nanowires. As for the Al_2O_3–coated GaN nanowires, our TEM and EDX line profiles reveal the cylindrical coating of Al_2O_3.

A excitonic PL band is remarkably enhanced around a hundred times in intensity when the surfaces of the GaN nanowires are oxidized, and that this PL band is strengthened in intensity, even when the surfaces of the GaN nanowires are coated with Al_2O_3. The enhancement of the PL intensity for the GaN nanowires with oxidized surface may be explained by the absence of the surface states within the GaN material. This PL study shows also that the Al_2O_3-coating passivates some of the surface states.

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REFERENCES

[1] T. Nishida, N. Kobayashi, and T. Ban, "GaN-free transparent ultraviolet light-emitting diodes", Appl. Phys. Lett., Vol. 82, p. 1, 2003.

[2] D. Walker, A. Saxler, P. Kung, X. Zhang, M. amilton, J. Diaz, and M. Razeghi, "Visible blind GaN p-i-n Photodiodes", Appl. Phys. Lett., Vol. 72, p. 3303, 1998.

[3] M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, "Catalytic growth of zinc oxide nanowires by vapor transport", Adv. Mater., Vol. 13, p. 113, 2001.

[4] H. Z. Zhang, Y. C. Kong, Y. Z. Wang, X. Du, Z. G. Bai, J. J. Wang, D. P. Yu, Y. Ding, Q. L. Hang, and S. Q. Feng, "Ga_2O_3 nanowires prepared by physical evaporation", Solid State Commun., Vol. 109, p. 677, 1999.

[5] L. J. lauhon, M. S. Gudlksen, D. Wang, and C. M. Lieber, "Epitaxial core–shell and core–multishell nanowire heterostructures", Nature, Vol. 420, p. 57, 2003.

[6] S. Pal, R. Mahapatra, S. K. Ray, B. R. Chakraborty, S. M. Shivaprasad, S. K. lahiri, and D. N. Bose, "Microwave plasma oxidation of gallium nitride", Thin solid films, Vol. 425, p. 20, 2003.

[7] L. H. Peng, C. H. Liao, Y. C. Hsu, C. S. Jong, C. N. Huang, J. K. Ho, C. C. Chiu, and C. Y. Chen, "Photoenhanced wet oxidation of gallium nitride", Appl. Phys. Lett., Vol. 76, p. 511, 2000.

[8] S. D. Wolter, B. P. Luther, D. L. Waltemyer, C. Onnby, S. E. Mohney, and R. J. Molnar, "X-ray photoelectron spectroscopy and x-ray diffraction study of the thermal oxide on gallium nitride", Appl. Phys. Lett., Vol. 70, p. 2156, 1997.

[9] N. J. Watkins, G. W. Wicks, and Y. Gao, "Oxidation study of GaN using x-ray photoemission spectroscopy", Appl. Phys. Lett., Vol. 75, p. 2602, 1999.

[10] H. Kim, S. J. Park, and H. Hwang, "Thermally oxidized GaN film for use as gate insulators", J. Vac. Sci. Technol. B., Vol. 19, p. 579, 2001.

[11] B. Lux, C. Colombier, and H. Altena, "Preparation of alumina coatings by chemical vapour deposition", Thin Solid Films, Vol. 138, p. 49, 1986.

[12] Y. Kim, S. M. Lee, C. S. Park, S. I. Lee, and M. Y. Lee, "Substrate dependence on the optical properties of Al_2O_3 films grown by atomic layer deposition", Appl. Phys. Lett., Vol. 71, p. 3604, 1997.

[13] W. S. Jeon, S. Yang, C. S. Lee, and S. W. Kang, "Atomic layer deposition of Al_2O_3 thin films using trimethylaluminum and isopropyl alcohol", J. Electrochem. Soc., Vol. 149, p. C306, 2002.

[14] A. Paranjpe, S. Gopinath, T. Omstead, and R. Bubber, "Atomic layer deposition of AlO_x for thin film head gap applications", J. Electrochem. Soc., Vol. 148, p. G465, 2001.

[15] Y. J. Lee and S.W. Kang, "Atomic layer deposition of aluminum thin films using an alternating supply of trimethylaluminum and a hydrogen plasma", Electrochem. Solid State Lett., Vol. 5, p. C91, 2002.

[16] J. S. Lee, M. I. Kang, S. Kim, M. S. Lee, Y. K. Lee, "Growth of zinc oxide nanowires by thermal evaporation on vicinal Si(1 0 0) substrate", J. Cryst. Growth, Vol. 249, p. 201, 2003.

[17] B. C. Kim, K. T. Sun, K. S. Park, K. J. Im, T. Noh, M. Y. Sung, S. Kim, S. Nahm, Y. N. Choi, and S. S. Park, "β-Ga_2O_3 nanowires synthesized from milled GaN powders", Appl. Phys. Lett., Vol. 80, p. 479, 2002.

[18] J. S. Lee, K. Park, S. Nahm, S. W. Kim, and S. Kim, "Ga_2O_3 nanomaterials synthesized from ball-milled GaN powders", J. Cryst. Growth, Vo. 244, p. 287, 2002.

[19] H. W. Seo, S. Y. Bae, J. Park, H. Yang, K. Park, and S. Kim, "Strained gallium nitride nanowires",J. Chem. Phys., Vol. 116, p. 9492, 2002.

[20] J. C. Chou, S. Y. Yang, and Y. S. Wang, "Study on the optoelectronic properties of amorphous selenium-based xerographic photoreceptors for electrophotography", Mater. Chem. Phys., Vol. 78, p. 666, 2003.

[21] C. I. Wu and A. Kahn, "Negative electron affinity and electron emission at cesiated GaN and AlN surfaces", Appl. Surf. Sci., Vol. 162-163 p. 250, 2000.

[22] T. Yoshida, T. Hashizume, and H. Hasegawa, "Characterization of interface electronic properties of low-temperature ultrathin oxides and oxynitrides formed on Si(111) surfaces by contactless capacitance-voltage and photoluminescence methods", Jpn. J. Appl. Phys., Vol. 36, p. 1453, 1997.