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Electronic structure of GaN nanowire studied by x-ray-absorption spectroscopy and scanning photoelectron microscopy

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X-ray absorption near edge structure (XANES) and scanning photoelectron microscopy (SPEM) measurements have been employed to obtain information on the electronic structures of the GaN nanowires and thin film. The comparison of the XANES spectra revealed that the nanowires have a smaller (larger) N (Ga) K edge XANES intensity than that of the thin film, which suggests an increase (decrease) of the occupation of N $2p$ (Ga $4p$) orbitals and an increase of the N (Ga) negative (positive) effective charge in the nanowires. The SPEM spectra showed that the Ga $3d$ band for the nanowires lies about 20.8 eV below the Fermi level and has a chemical shift of about -0.9 eV relative to that of the thin film. © 2003 American Institute of Physics.
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Gallium nitride (GaN) is a promising material for applications in light emitting and laser diodes as well as in high temperature and high power electronic devices.¹ In particular, one-dimensional (1D) GaN nanowires have recently attracted much research interest in materials science.² Studies of GaN nanowires can be used to gain insights into the fundamental aspects of 1D physical properties and its application as optoelectronic nanodevices.³ The synthesis and morphology of nanometer-scale GaN has been investigated previously.^{4–6} The electronic structure of a nanometer-scale material is expected to differ from that of the bulk material.^{7,8} In the present study, x-ray absorption near edge structure (XANES) measurements at the N and Ga K -edges and Ga L_3 -edge and scanning photoelectron microscopy (SPEM) measurements have been performed to understand the electronic structures of the GaN nanowires and thin film.

N K -, Ga L_3 -, and K -edges XANES measurements were performed at the high-energy spherical grating monochromator and Wiggler-C beamlines, respectively, and SPEM measurements were executed at the U5 undulator beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The SPEM-end station of the NSRRC has been described elsewhere.⁹ Details of the preparation and characterization for GaN nanowires can be found elsewhere.^{5,6} The reference GaN thin-film epilayer sample with a hexagonal (wurtzite) structure was grown on an

Al_2O_3 (0001) substrate.¹⁰ From scanning electron microscope (SEM) and transmission electron microscope (TEM) measurements, the GaN nanowires were found to be several microns long and 16–24 nm in diameter as shown in Fig. 1(a). They were characterized to have a hexagonal (wurtzite) structure as displayed in Fig. 1(b).

Figures 2(a) and 2(b) exhibit the XANES spectra of the GaN nanowires and the reference GaN thin film at the N and Ga K -edges, respectively. Features A_1-D_1 and A_2-D_2 are related to the four features of the calculated N (Ga) derived p partial density of states.¹¹ These features agree well with the σ bond (bilayer bond) and the π bond (c -axis bond) XANES spectra of GaN films obtained previously.^{12,13} The overall spectral line shapes of both N and Ga K -edges XANES spectra of the GaN nanowires and thin film exhibit similar features. However, the intensities of the features A_1-D_1 in the N K -edge XANES spectrum of the nanowire are noticeably smaller than those of the thin film as shown in Fig. 2(a). This result indicates a decrease in the number of unoccupied N $2p$ states in the nanowire, which implies an increase of the occupation of N $2p$ orbitals and an increase of the negative effective charge on N ions. In Fig. 2(b), the intensity of feature B_2 (C_2) in the Ga K -edge spectrum of the nanowire is clearly larger (smaller) than that of the thin film. While the intensities of features A_2 and D_2 for the nanowire and thin film are fairly similar. The enhancement of feature B_2 and depression of feature C_2 suggest an overall shift of the Ga $4p$ derived states toward lower energies in the nanowire and an increase of the attractive electrostatic potential on Ga

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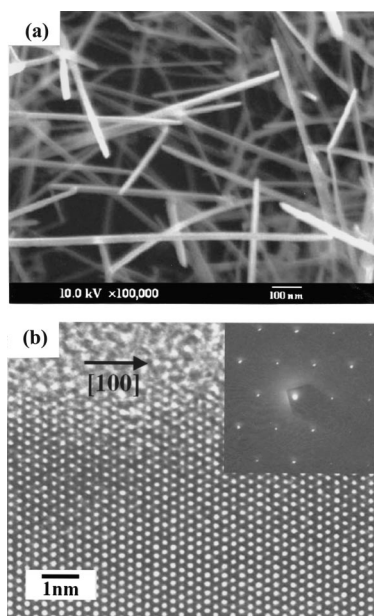


FIG. 1. (a) SEM image and (b) high-resolution TEM image and its corresponding electron diffraction (inset) of GaN nanowires.

ions. The overall intensity of the Ga K -edge XANES spectrum of the nanowire is larger than that of the thin film, which suggests a slight increase of the positive effective charge consistent with the increase of the negative effective charge on N ions implied by N K -edge spectra.

Figure 3 presents the Ga L_3 -edge XANES spectra of the GaN nanowire and thin film. Ga L_3 -edge XANES probes the unoccupied s and d derived states. Chiou *et al.* showed that the Ga L_3 -edge XANES spectrum of the GaN thin film is insensitive to the photon incident angle¹² suggesting that the states contributing to the spectrum be primarily s -like. This result also agreed with calculations by Lawniczak-Jablonska *et al.*, which showed that the states near the conduction band minimum do not have significant contribution from Ga d -orbitals.¹¹ GaN is a relatively ionic material. If the

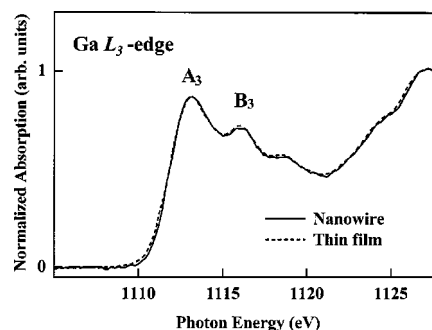


FIG. 3. Normalized Ga L_3 -edge absorption spectra of GaN nanowires and thin film.

Ga–N bond would be pure ionic without any covalent contribution, Ga $4s$ and $4p$ orbitals are expected to be completely empty. In this case, its three $4s$ and $4p$ valence electrons move to N, so that Ga and N become Ga^{3+} and N^{3-} ions, respectively. In the real case, the Ga–N bond has a partial covalent character and the valence band of GaN contains a small fraction of Ga $4s$ - and $4p$ -derived states. The majority of the Ga $4s$ - and $4p$ -derived states are in the conduction band. Thus, the Ga $4s$ -derived states will contribute dominantly to feature A_3 . Since conduction s and p bands are wide bands, feature B_3 and the spectrum in the higher-energy region may be attributable to a mixture of Ga $4s$ -derived states and other higher energy states which have s and/or d components projected on the Ga ion, for example Ga $5s$ and $4d$ and higher-energy Ga–N hybridized states. Figure 3 shows that the Ga L_3 -edge XANES spectrum of the nanowire almost coincides with that of the thin film, which may be attributed to the itinerant nature and environment insensitivity of these states.

Figures 4(a) and 4(b) display Ga $3d$ core-level and valence-band photoemission spectra of the GaN nanowires and thin film. The upper and lower insets in Fig. 4(a) are the SPEM images from the Ga $3d$ signal of the nanowire and thin film samples, respectively, measured from topview. The maximum intensities are in the bright area corresponding to a bunch of GaN nanowires. The spectra shown in Figs. 4(a) and 4(b) are photoelectron yields from regions marked as A, B, and C of the nanowires and from regions marked as D and E of the thin film. The zero energy in Fig. 4(a) is chosen at the Fermi level, E_F , of the GaN thin film, which is the threshold of the thin film's emission spectrum. The general line shapes of the valence-band spectra of the GaN thin film as shown in Fig. 4(a) agree with those obtained previously from the photoemission measurements of bulk GaN.^{10,14,15} There are two main features (A_4 and B_4) in the valence-band SPEM spectra, which were attributed primarily to the Ga $4p$ –N $2p$ and Ga $4s$ –N $2p$ states with the N $2p$ states dominating the top of the valence band.^{16–18} The main features A_4 and B_4 in the spectra of the nanowires are broader and less resolved and feature A_4 apparently shifts to higher binding energies relative to that of the thin film. Figure 4(a) reveals that the intensities of the nanowire valence-band SPEM spectra are apparently smaller than that of the thin film. The valence-band SPEM intensity is proportional to the density of valence-band states, transition probability from the valence-band states to the continuum states, the photon absorption cross-section areas of electrons in the valence-

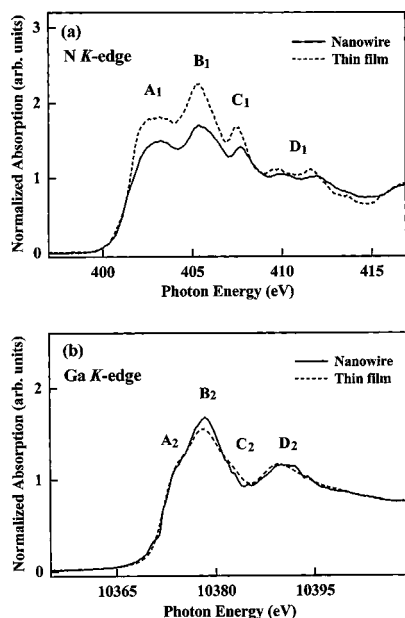


FIG. 2. (a) Normalized N K -edge and (b) Ga K -edge absorption spectra of GaN nanowires and thin film.

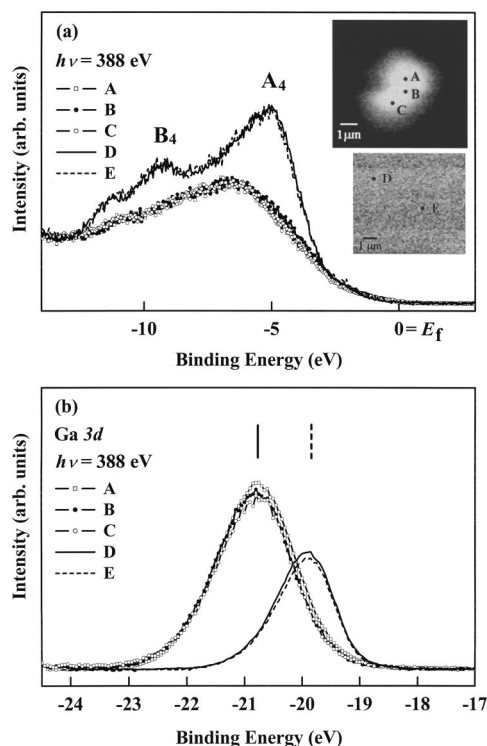


FIG. 4. (a) Valence-band and (b) Ga 3d core-level SPEM spectra from regions marked as A–E shown in the insets, which present the SPEM Ga 3d images of a bunch of nanowires (upper inset) and thin film (lower inset).

band states, and geometric factors. Since the initial states involved in the XANES measurements are core states, which are highly localized within the atoms, the relative intensities of the XANES spectra better represent relative densities of states than those of the valence-band SPEM spectra. Then, the apparent depression of the SPEM intensity for the nanowires cannot be interpreted as a decrease of the density of valence-band states because it is inconsistent with the N K-edge XANES results that indicate an enhancement of the N 2*p*-orbital occupation in the nanowires. Since valence-band states are relatively extended, the cross-section areas of the electrons in the valence-band states in the thin film can be expected to be larger than those in nanowires, which may be the cause of the apparent larger SPEM intensities for the thin film.

The full width of half maximum of the features in the Ga 3d SPEM spectra of the nanowires are about 1.6 eV, which are larger than those of the thin film of about 1.2 eV as shown in Fig. 4(b). The broadening of the Ga 3d features in the SPEM spectra of the nanowires suggest a stronger coupling between Ga 3d orbitals and N 2*s* and 2*p* orbitals. The main features of the nanowires shift to lower energies by about 0.9 eV. The shifts of the Ga 3d feature and the two valence-band main features that contain contributions from Ga orbitals to lower energies relative to those of the thin film can be attributed to a larger positive effective charge at the Ga site, a larger work function, or the change in the local electrostatic polarization. The first one is compatible with the N K- and Ga K-edge results, which indicate a slight increase of the negative (positive) effective charges on N (Ga) ions. Meanwhile, the differences in the work function and/or local electrostatic polarization, which depend strongly on the surface geometry and polarization due to the polar nature of

GaN,¹⁹ between the nanowire and thin film may also be the cause of these chemical shifts.

The main features of the nanowires located about −20.8 eV as shown in Fig. 4(b) have much larger intensities than those of the thin film. The Ga 3d SPEM intensity is proportional to the density of Ga 3d states, transition probability from the Ga 3d states to the continuum states, the photon absorption cross-section areas of electrons in the Ga 3d states, and geometric factors. Since the integration of the density of Ga 3d states is 5 per Ga atom (i.e., the number of *d* orbitals) without spin degeneracy, which is the same for both the nanowires and thin film, the much larger Ga 3d SPEM intensities for the nanowires suggest that those factors unrelated to the density of 3d states be much larger for the nanowires than for the thin film. The broadening of the Ga 3d energy band stated previously indicates an increase of the degree of delocalization of the Ga 3d orbitals in the nanowires, which suggests that the cross-section areas of the 3d electrons in the nanowires are increased. The transition probabilities are also enhanced in the nanowires because the overlap integrals between Ga 3d orbitals and the continuum states are increased.

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