

Electronic structures of group-III–nitride nanorods studied by x-ray absorption, x-ray emission, and Raman spectroscopy

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Nitrogen (N) and metal (Al, Ga, and In) *K*-edge x-ray absorption near-edge structure (XANES), x-ray emission spectroscopy (XES), and Raman scattering measurements were performed to elucidate the electronic structures of group-III–nitride nanorods and thin films of AlN, GaN, and InN. XANES spectra show slight increase of the numbers of unoccupied N *p* states in GaN and AlN nanorods, which may be attributed to a slight increase of the degree of localization of conduction band states. The band gaps of AlN, GaN, and InN nanorods are determined by an overlay of XES and XANES spectra to be 6.2, 3.5, and 1.9 eV, respectively, which are close to those of AlN and GaN bulk/films and InN polycrystals. © 2006 American Institute of Physics.

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Group-III–nitrides such as AlN, GaN, and InN have attracted substantial interest because of their potential technological applications.^{1–5} Recently, one-dimensional (1D) nanostructures of these materials have been synthesized for potential applications in field emission devices.^{6–10} Group-III–nitrides are chemically and mechanically stable and exhibit low electron affinities.^{6,9} They are therefore of particular value in device applications and the knowledge of the electronic structures of these 1D materials will be important. The development of these 1D nanostructures is relatively new and few studies of their electronic structures have been conducted,^{11,12} although more studies have been performed for films/bulk materials.^{13–18} This work focuses on the measurements of the electronic properties of AlN, GaN, and InN nanorods using Raman scattering, x-ray absorption near-edge structure (XANES), and x-ray emission spectroscopy (XES) techniques.

N, Al, Ga, and In *K*-edge XANES measurements were carried out at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. XES and corresponding XANES measurements of the N *2p* states were carried out at the Advanced Light Source, Lawrence Berkeley National Laboratory. AlN, GaN, and InN nanorods were grown on the Si (100) substrate by chemical vapor deposition (CVD). The

details of the preparation are presented elsewhere.^{7,8,10} Figure 1 displays the x-ray diffraction (XRD) data of the nanorods and the corresponding films. These data demonstrate that all of the compounds crystallize in a hexagonal (wurtzite) structure. Both nanorods and films almost have the same lattice constants within the experimental error limits. Figure 1 shows that InN nanorods contain some indium metal clusters. The films were also grown by CVD on the Si substrate, except for the GaN film, which was grown on the Al₂O₃ (0001) substrate. The GaN nanorods and films exhibit the characteristic peak of the hexagonal (wurtzite) structure with

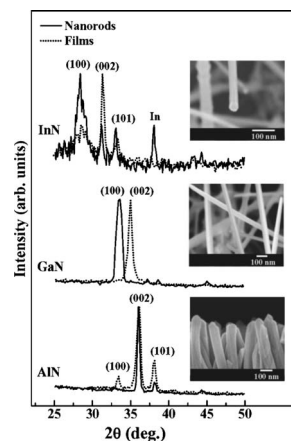


FIG. 1. X-ray diffraction patterns of nanorods and their corresponding thin films of AlN, GaN, and InN. The inset presents SEM images of nanorods.

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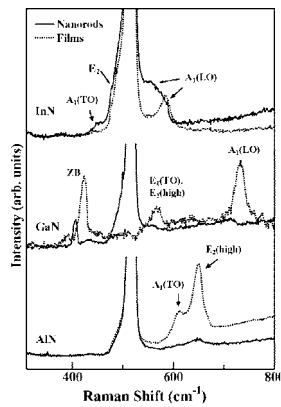


FIG. 2. Raman spectra of AlN, GaN, and InN nanorods and their corresponding thin films.

(100) and (002) preferential orientations, respectively. The scanning electron microscopy (SEM) images in the insets of Fig. 1 show that InN and GaN nanorods are randomly oriented, while AlN nanorods are quasialigned along the c axis. The diameters of InN and GaN nanorods are ranged from 30 to 100 nm whereas the average diameters of AlN nanorods are ~ 100 nm with lengths of ~ 750 nm.

Figure 2 presents Raman spectra of InN, GaN, and AlN nanorods and corresponding films. The features located at about 520 cm^{-1} , whose tops have been cut off, is the Raman mode of the Si substrate. Raman modes, such as (A_1) longitudinal optical (LO), A_1 and E_1 transverse optical (TO), E_2 (high), and zone boundary (ZB) modes are close to those of the bulk systems reported elsewhere.^{8,10,19,20} The features in all the Raman spectra of the nanorods of these three nitrides are much broader and weaker than those of the films. The Raman modes of the nanorod samples exhibit asymmetric line shapes and shift to lower frequencies relative to those of thin films, except AlN. The shifts to lower frequencies and asymmetric broadened Raman lines in nanostructures were attributed to size effects.^{10,19}

Figure 3 displays the N K -edge XANES spectra of InN, GaN, and AlN nanorods and the films. The spectral features of the three compounds are similar except some minor differences, especially in peaks denoted by A_1 – D_1 . The N K -edge XANES features are contributed by unoccupied N $2p$ -derived states and the states of neighboring cations, which have significant p -symmetry components projected onto the N sites.^{21–23} In the hexagonal (wurtzite) structure of

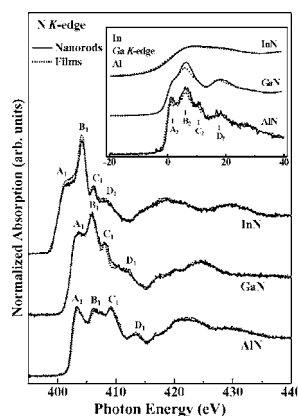


FIG. 3. N K -edge XANES spectra of AlN, GaN, and InN nanorods and their corresponding thin films. The inset displays metal (Al, Ga, and In) K -edge XANES spectra of nanorods and their corresponding thin films. Energy of metal K -edge is offset to 0 eV.

group-III–nitrides, there are two distinct types of N-metal bonds. One is along the c axis, which is called the π -(p_z) bond, and another lies in the ab plane, which is called the σ -(p_{xy}) bond.^{11–13} These π - and σ -bond states dominate the first four features (A_1 – D_1).^{11–15} The present XANES features of all the three compounds are very similar to those of the σ -bond spectra reported earlier,¹³ i.e., the A_1 – C_1 features have similar intensities for AlN and feature B_1 has the strongest intensity for GaN and InN. These spectra clearly show different trends of the π -bond features from those obtained by polarized measurements,¹³ in which feature B_1 had a much lower intensity and feature A_1 had the largest intensity for AlN, while feature C_1 had the largest intensity for GaN and features B_1 and C_1 have similar intensities for InN. Another important observation is that the N K -edge in InN (both nanorods and film) is shifted downward in energy by approximately 2.4 eV lower than those of GaN and AlN, whose N K -edges are very close to each other. The origin of this shift overall can be interpreted as a narrowing of the energy gap relative to those of GaN and AlN compounds.

The inset in Fig. 3 shows Al, Ga, and In K -edge XANES spectra for nanorods and films. The zero energy shown in the inset corresponds to the absolute energies of 1562.3, 10369.5, and 27938.9 eV, for the Al, Ga, and In K edges, respectively. The nanorod and film spectra are similar to each other and the overall spectral features of AlN and GaN are close to those reported elsewhere for bulk films.^{11–18} Al K -edge XANES spectrum has four distinctive features A_2 – D_2 , which was argued to be due to split of the unoccupied Al $3p$ band by the crystal field.^{21–23} Ga K -edge spectrum can be resolved into three features, while the In K -edge spectrum has only one very broad feature within the 40 eV range. This trend shows that the degree of the broadening of the cation valence p bands increases with the size of the cations, which also correlates with the trends of the decrease of the effective masses or increase of the conduction band width in the order of Al, Ga, and In. The intensities of feature B_2 in GaN and A_2 – C_2 in AlN are slightly larger for nanorods than for films, which may be intuitively interpreted as a slight increase of the numbers of unoccupied Ga $4p$ and Al $3p$ states for GaN and AlN nanorods. This interpretation implies a slight increase of the positive effective charge on the cations and a corresponding slight increase of the electron charge on the N ions. However, this is inconsistent with the N K -edge results. Thus, the slight increase of the cation K -edge XANES intensities for the nanorods should be interpreted as an increase of the degree of localization of the cation p orbitals due to the confinement of the nanorod surfaces that slightly shrinks the p -band width and shift some higher energy states to the lower-energy area. The insensitivity in the InN case is due to a much broader In p band. Notably, it is well known that electron core-hole lifetimes are important to the excitation of absorbing atoms, especially in the exciting atoms with higher atomic numbers,²⁴ such as In atoms, so the larger electron core-hole lifetimes and experimental uncertainties are also responsible for the broadening of the In K -edge XANES features of InN compounds.

Figure 4 presents the XES and corresponding N K -edge XANES spectra of nanorods and films of all three compounds. The XES of all three compounds show that the valence band has two features in consistent with theoretical calculations for respective bulk systems.^{21–23} It is well known that the occupied states in the vicinity of the valence

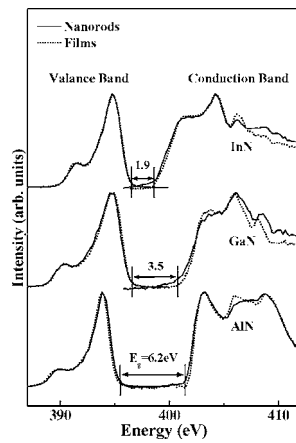


FIG. 4. XES and corresponding XANES spectra of N $2p$ states of nanorods and films.

band maximum (VBM) are dominantly anion, i.e., N, valence p states, while the unoccupied states in the vicinity of the conduction band minimum (CBM) are cation valence s states. The leading edge of the XES spectra can be interpreted as VBM. The N K -edge XANES spectra measures p -symmetry states centered at the N ion by the dipole transition selection rule, which are composed of the unoccupied N $2p$ states and the s -, p -, and even d -orbital states of neighboring cations, which have significant projection of p -symmetry components on the N sites.²⁵ Due to the much larger sizes of Al, Ga, and especially In ions relative to that of the N ion, the valence s orbitals of Al, Ga, and In ions, which constitute the near-CBM states, are expected to extend deep into the N ions and have substantial p -symmetry components on the N sites. Thus, the leading edge of the N K -edge XANES spectra can be interpreted as CBM. Then, the gaps between XES and N K -edge XANES spectra shown in Fig. 4 can be interpreted as the band gaps, which are 1.9, 3.5, and 6.2 eV, respectively, for InN, GaN, and AlN. The band gaps of AlN and GaN shown in Fig. 4 are close to those reported previously.^{1,2}

As for InN, the 1.9 eV band gap is close to those reported for polycrystalline InN. However, it is about twice larger than those reported for single-crystal high-quality InN films, typically between 0.6 and 0.9 eV by photoluminescence (PL) measurements.^{5,26,27} Variations in the apparent color and PL spectra of the InN nanorods were also observed.⁸ For the optically brown InN nanorods having diameters in the range of 30–50 nm, the PL study showed a peak at 1.9 eV. By contrast, for the optically black InN nanorods having diameters in the range of 50–100 nm, the PL peak appeared at around 0.77 eV. The wide range of measured band gaps of InN has caused confusion and controversy in understanding the electronic property of InN. The high-quality single-crystal InN films are grown along the c axis, so that these films are polar films formed by In–N dipolar arrays, which may give rise to internal electric field that tilts the energy bands. For x-ray photons, the wavelengths and the sizes of their wave packets are in the order of angstrom; the band tilt has no effect on the measured band gap. By contrast, the ~ 0.8 eV photons involved in PL measurements have wavelengths of ~ 1 μm , which implies that the spatial extent of these photons may be large, so that the electron and hole states involved in photon emission or absorption can have a spatial separation, say, Δz . In this case the photon energy will be the fundamental gap minus Δz

times the slope of the band tilt. The slope of the band tilt depends on the film thickness or the diameter/length ratio of the nanorod,²⁸ which may explain why a wide range of apparent band gaps between 0.6 and 0.9 eV have been observed for single-crystal c -axis oriented InN films by PL or similar optical measurements.

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