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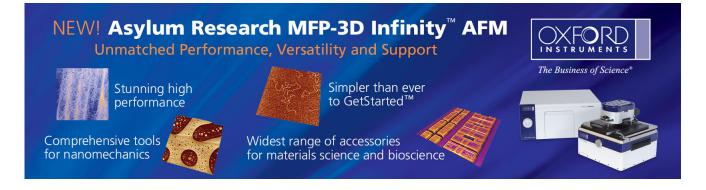

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Band structure and fundamental optical transitions in wurtzite AlN

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With a recently developed unique deep ultraviolet picoseconds time-resolved photoluminescence (PL) spectroscopy system and improved growth technique, we are able to determine the detailed band structure near the Γ point of wurtzite (WZ) AlN with a direct band gap of 6.12 eV. Combined with first-principles band structure calculations we show that the fundamental optical properties of AlN differ drastically from that of GaN and other WZ semiconductors. The discrepancy in energy band gap values of AlN obtained previously by different methods is explained in terms of the optical selection rules in AlN and is confirmed by measurement of the polarization dependence of the excitonic PL spectra. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1633965]

AlN, with a direct band gap exceeding 6 eV, is emerging as an important semiconductor.[1–3] AlN and Al-rich AlGaN alloys, covering wavelengths from 300 to 200 nm, are ideal materials for the development of chip-scale UV light sources/sensors. Efficient UV light sources/sensors are crucial in many fields of research. Protein fluorescence is generally excited by UV light; monitoring changes of intrinsic fluorescence in a protein can provide important information on its structural changes.[4] UV light sources combined with fluorescent phosphors are also important in current pursuit of producing solid-state white light emitting devices.[5]

Besides important practical applications, AlN is also a unique semiconductor compound for fundamental studies. In contrast to all the other II–VI and III–V binary semiconductors, AlN in the zinc-blende structure has a larger band gap than that in the wurtzite (WZ) structure.[6] AlN is also the only WZ semiconductor compound that has been predicted to have a negative crystal field splitting at the top of valence band.[7,8] Confirmation of these predictions are important because the negative crystal field splitting can lead to unusual optical properties of AlN than other wurtzite semiconductors such as GaN.[9]

Our knowledge concerning the band structure and optical properties of AlN is very limited. For example, the detailed band structure parameters near the Γ point of AlN are still unclear. The band gap was determined in the past only by optical absorption and transmission measurements with energy values scattered around 6.3 eV at liquid helium temperatures.[10] The band structure parameters, including the effective masses of electrons and holes as well as the character and splitting at the valence band edge are not yet well understood.[7,11] Fundamental optical transitions including the band-to-band and excitonic transitions have not been well investigated. It is, therefore, of fundamental and technological importance to fill in the unknowns for AlN.

Recently, progress have been made for the growth of AlN epilayers.[1–3] It has been demonstrated that AlN epilayers with high optical qualities comparable to those of GaN

can be achieved.[1] In this letter, we report the properties of the fundamental optical transitions in AlN probed by photoluminescence (PL) spectroscopy measurements. By comparing the experimental results with first-principles calculations, we are able to provide a coherent picture for the band structure parameters of wurtzite AlN near the Γ point. The results reveal significant differences between AlN and GaN in their band structure parameters, and hence, their fundamental optical properties. Our results explained the puzzling discrepancy in energy band gap values of AlN obtained previously by different methods.[10]

The 1-μm-thick AlN films were grown by metalorganic chemical vapor deposition on sapphire (0001) substrates with low temperature AlN nucleation layers. Trimethylaluminum and NH_3 were used as Al and N sources, respectively. The deep-UV laser spectroscopy system used for PL studies consists of a frequency quadrupled 100 fs Ti:sapphire laser with an excitation photon energy set around 6.28 eV (with a 76 MHz repetition rate and a 3 mW average power), a 1.3 m monochromator, and a streak camera (2 ps time resolution) with a detection capability ranging from 185 to 800 nm.[12] Figure 1 shows typical temperature dependent band edge PL emission spectra for AlN. At 10 K, two emission lines at 6.033 and 6.017 eV are resolved. Based on time-resolved[13] and temperature dependent PL studies, as well as their light polarization dependence (discussed later), these emissions are attributed to the free A-exciton (FX) and its associated neutral donor bound (I_2) exciton transitions, respectively. As the temperature increases, the relative intensity of the I_2 transition peak at 6.017 eV decreases, while that of the FX transition at 6.033 eV increases, which resembles the behavior of I_2 and FX seen in GaN.[14] This is expected because the donor bound excitons dissociate at higher temperatures into FX and neutral donors D^0, ($D^0X \rightarrow FX + D^0$).

Figure 2 shows the Arrhenius plot of the PL intensity of the FX transition line at 6.033 eV. The solid line in Fig. 2 is the least squares fit of the measured data to Eq. (1), which describes the thermal dissociation (activation) of free excitons
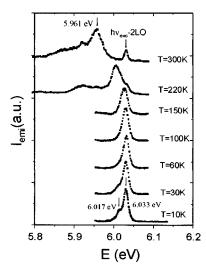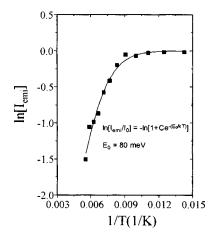
$$I_{emi}(T) = I_0 [1 + Ce^{(-E_0/kT)}]^{-1}, \tag{1}$$

FIG. 1. PL spectra of AlN epilayer measured at different temperatures between 10 and 300 K. An additional weak emission line indicated as $h\nu_{exc}$-2LO that becomes visible at room temperature is due to the Raman scattering of the excitation laser line with two longitudinal optical phonons (2LO).

FIG. 3. Calculated band structure of wurtzite AlN near the Γ point. At $k = 0$, the top of the valence band is split by crystal field and spin orbit coupling into the $\Gamma_{7vbm}(A)$, $\Gamma_{9v}(B)$, and $\Gamma_{7v}(C)$ states. The sign $\perp$ ($\parallel$) denotes the direction perpendicular (parallel) to the c axis of the AlN epilayer. The A band exciton binding energy is denoted as E_x^A.

where $I_{emi}(T)$ and I_0 are, respectively, the PL intensities at a finite temperature T and 0 K, while E_0 is the activation energy, i.e., the free exciton binding energy E_x, in AlN. A binding energy of $E_0 = 80$ meV is obtained from the fitting, which agrees with the value determined from the temperature dependence of the FX decay lifetime.[13] The energy gap at 10 K is thus 6.033 eV $+$ 0.080 eV $=$ 6.11 ($\pm$0.01) eV. This value is consistent with the value derived from another experiment[2] and a recent theoretical prediction.[6]

To gain the insights of the detailed band structure parameters near the Γ point, we have performed first-principles band structure calculations for WZ AlN at the experimental lattice constants. We use the local density approximation as implemented by the all-electron, relativistic, WIEN2K code.[15] The calculated band structure together with the measured band gap and exciton binding energy are shown in Fig. 3. Comparing with the band structure of GaN,[9] the most significant difference is the negative crystal-field splitting Δ_{CF} (-219 meV) in AlN instead of a positive value ($+38$ meV) in GaN. We find that this is because AlN, being more ionic, has a much smaller c/a ratio (1.601 vs 1.626 for
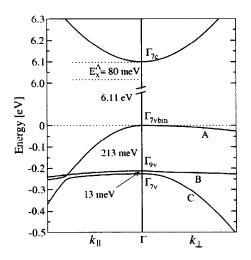
GaN) and a much larger u parameter (0.3819 vs 0.3768 for GaN). Here, u is a dimensionless cell-internal coordinate that distinct the two nearest-neighbor anion-cation bond lengths in WZ structure. For an ideal WZ structure with $c/a = \text{sqrt}(8/3)$ and $u = 0.375$ the two bond lengths are equal. Neglecting this effect in calculations can lead to large errors.[7] This larger structural distortion in AlN also explains why WZ AlN has a smaller band gap than ZB AlN, whereas for all the other binary semiconductors the opposite trend exists.[16]

There are many important consequences of this large negative Δ_{CF} in AlN. First, the order of the valence bands in AlN is different from that of GaN. The valence bands, given in increasing order of their transition energies, are $\Gamma_{7vbm}(A)$, $\Gamma_{9v}(B)$, $\Gamma_{7v}(C)$ for AlN, whereas in GaN the order is Γ_{9vbm}, Γ_{7v}, Γ_{7v}.[9] Because of the large energy separation between the valence band maximum and the second and third valence states (Fig. 3), fundamental optical transitions near the Γ point, as well as the transport properties of the free holes in AlN, are predominantly determined by the top Γ_{7vbm} band instead of the top Γ_{9vbm} band in GaN. Second, the optical properties of AlN differ significantly from GaN. Table I lists the calculated square of the dipole transition matrix elements $I = |\langle \psi_v | \mathbf{p} | \psi_c \rangle|^2$ between the conduction state and the three valence states at Γ of WZ AlN for lights polarized parallel ($\parallel$) and perpendicular ($\perp$) to the c axis. For an arbitrary light polarization, the matrix element $I(\theta) = \cos^2 \theta \, I(E\|c) + \sin^2 \theta \, I(E\perp c)$, where E denotes the electric field component of the light and θ is the angle between E and the c axes. Our results show that the recombination between the conduction band electrons and the holes in the top most

FIG. 2. The Arrhenius plot of PL intensity [$\ln(I_{emi})$ vs $1/T$] for AlN epilayer. The solid line is the least squares fit of data to Eq. (1), from which a free exciton binding energy of 80 meV is obtained.

TABLE I. Calculated square of the dipole transition matrix elements I (in a.u.) of WZ AlN for light polarized parallel ($\parallel$) and perpendicular ($\perp$) to the c axis.

Transition	$I(E\|c)$	$I(E\perp c)$
$\Gamma_{7c} \leftrightarrow \Gamma_{7vbm}$	0.4580	0.0004
$\Gamma_{7c} \leftrightarrow \Gamma_{9v}$	0	0.2315
$\Gamma_{7c} \leftrightarrow \Gamma_{7v}$	0.0007	0.2310

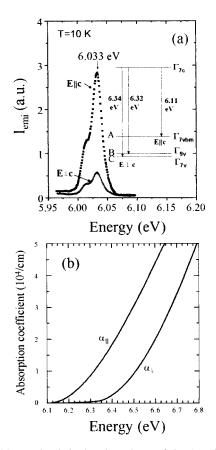Appl. Phys. Lett., Vol. 83, No. 25, 22 December 2003

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FIG. 4. (a) Measured polarization dependence of the A-exciton emission spectra of AlN. The inset shows the selection rules for the optical transitions at Γ in AlN. (b) Calculated absorption coefficients $\alpha_\perp$ and $\alpha_\parallel$ of AlN for light polarization $E\perp c$ and $E\parallel c$.

4(a), the transition between the Γ_{7c} and the top valence band Γ_{7vbm}, which determines the minimum energy gap of AlN, is not active for $E\perp c$. Therefore, this type of optical measurement cannot obtain the true fundamental band gap of AlN. Instead, it measures the energy gap between the conduction band and the B (or C) valence band because these transitions are active for α polarization. This explains why larger band gaps, about 6.3 eV, were reported in earlier measurements,[10] whereas the value of 6.11 ± 0.01 eV is obtained here by PL. This is in contrast to the case for GaN epilayers, in which the emission to the top most valence band is allowed for α polarization.[9,17] Thus, different optical measurements would generally yield the same band gap value in GaN.[10]

To further confirm the earlier interpretation, we have calculated the absorption coefficients for AlN with two different light polarization directions, $E\perp c$ and $E\parallel c$. The results are shown in Fig. 4(b), which clearly show that optical measurements with polarization orientation of $E\perp c$, would reveal an apparent energy gap of $E_g+\Delta_{AB}\approx6.3$ eV that is about 0.2 eV larger than the minimum energy gap.

In summary, fundamental optical transitions and band parameters of AlN near the Γ point have been investigated by deep UV PL measurements together with first-principles band structure and absorption spectrum calculations. The results have revealed significant differences in the band structures between AlN and other binary WZ semiconductors. The origin of the puzzling band gap differences in AlN obtained by various measurements is explained through the optical selection rules for near band edge transitions in AlN.

valence state (Γ_{7vbm} or A) is almost prohibited for $E\perp c$, whereas the recombination between the conduction band electrons and holes in the (Γ_{9v} or B) and (Γ_{7v} or C) valence bands are almost forbidden for $E\parallel c$, as is shown schematically in the inset of Fig. 4(a). This is in sharp contrast to GaN in which the theoretical and experimental results have shown that the recombination between the conduction band electrons and the holes in the top most valence band (Γ_{9vbm} or A) is almost prohibited for $E\parallel c$.[9,17]

To confirm this unusual band structure in AlN, we have measured the polarization dependence of the A-exciton emission lines in AlN. To do so, a polarizer was placed in front of the entrance slit of the monochromator, so that the PL emission with either $E\perp c$ or $E\parallel c$ was collected. Figure 4(a) presents a comparison of the emission spectra of an AlN epilayer obtained for $E\perp c$ and $E\parallel c$. It conclusively demonstrates that the free A exciton and the associated bound-exciton transitions are almost prohibited for $E\perp c$, consistent with the present theoretical calculation.

Our understanding of the AlN band structure can be used to nicely explain some puzzling experimental data for AlN, such as the strong dependence of the measured band gap on the details of the experiments. The c axis of nitride films grown epitaxially is always parallel to the crystal growth direction. In many optical measurements such as absorption, transmission, and reflectance, the propagation direction k of the excitation light is generally parallel to the c axis and the light is, thus, polarized perpendicular to the c axis, $E\perp c$ (the so called α polarization). As illustrated in the inset of Fig.

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