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Citation: Appl. Phys. Lett. **99**, 021903 (2011); doi: 10.1063/1.3610469
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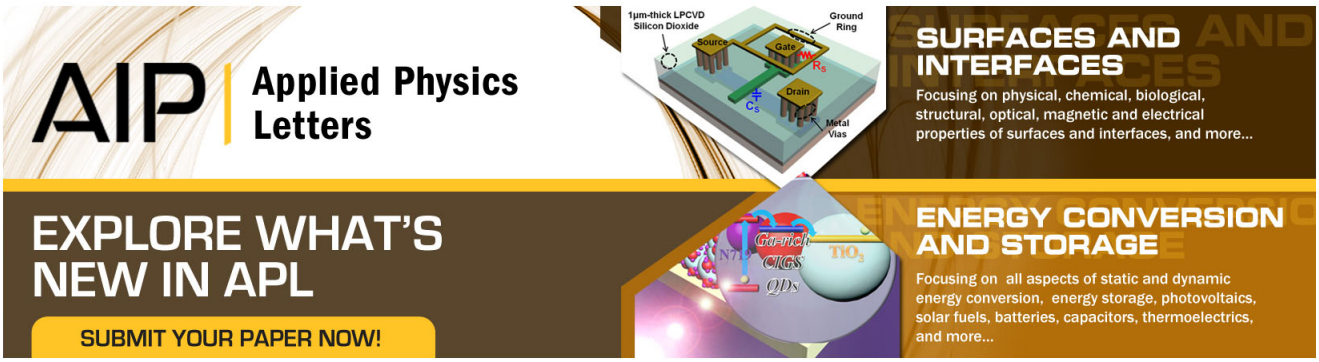

Synchrotron-based photoluminescence excitation spectroscopy applied to investigate the valence band splittings in AlN and $Al_{0.94}Ga_{0.06}N$

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(Received 18 April 2011; accepted 22 June 2011; published online 12 July 2011)

We demonstrate that synchrotron-based photoluminescence excitation (PLE) spectroscopy is a versatile tool for determining valence band splittings of AlN and high aluminum content AlGaN. PLE results are independently confirmed by synchrotron-based spectroscopic ellipsometry. The splittings between the ordinary and the extraordinary absorption edges are found to be −240 meV and −170 meV for AlN and $Al_{0.94}Ga_{0.06}N$, respectively. These values differ from the crystal field energy due to residual strain. © *2011 American Institute of Physics*. [doi:10.1063/1.3610469]

AlGaN alloys in the hexagonal wurtzite structure are considered as promising materials for the development of luminescence and laser diodes as well as solar-blind photodetectors operating in the ultraviolet (UV) spectral region. Despite intense research work, the optical properties around the band gap are not well understood yet. Transitions, both in absorption and emission, are governed by the lowest conduction band (CB) and the highest valence bands (VBs). These VBs are split into three subbands for wurtzite symmetry. In quasi-cubic approximation, the splittings can be described by the crystal field energy Δ_{cf} and the spin-orbit coupling Δ_{so}. These parameters are only determined for the binaries yet: $\Delta_{cf} = 9$ meV for GaN (Ref. 1), −212 to −230 meV for AlN (Refs. 2 and 3) and $\Delta_{so} = 19$ meV for GaN (Ref. 1), 16 meV for AlN (Ref. 2). From highest to lowest, this yields a VB order of Γ_9^v, Γ_{7+}^v, and Γ_{7-}^v for GaN, but Γ_{7+}^v, Γ_9^v, and Γ_{7-}^v for AlN. For the ternary alloy AlGaN, a change of sign of Δ_{cf} must result in a crossing of VBs of different symmetry character as indicated in Fig. 1. The exact spacings of the valence subbands can be calculated in the frame of **kp** perturbation theory.[4]

In case of (0001) orientation of the surface, the electric dipole interband transition between the CB (with Γ_7^c symmetry character) and the VB with Γ_9^v character is allowed for light impinging normal to the surface (i.e., with $\mathbf{E}\perp\mathbf{c}$). Bowing parameters for this transition are consistently reported as $0.5\ \text{eV} < b < 1\ \text{eV}$.[5–9] In contrast, the transition between CB and VB with Γ_{7+}^v character has vanishing oscillator strength for the electric field vector perpendicular to the c-direction ($\mathbf{E}\perp\mathbf{c}$) of III-nitrides when $\Delta_{cf} < -50$ meV. This means that the emission from the CB to the highest VB is hard to detect for high aluminum content AlGaN for light normal to the c-surface. Therefore, the dependence of Δ_{cf} on the aluminum content is not safely known yet. The VB crossing (Fig. 1) is predicted for about 5% aluminum for unstrained bulk AlGaN, if Δ_{cf} is linearly interpolated between GaN and AlN. This is in contradiction to experimental values determined mostly by polarization sensitive luminescence experiments, which find (for strained samples and quantum wells) the VB crossing between 25% (Ref. 10) and 81% (Ref. 11) aluminum. Generally, nonlinear dependency of Δ_{cf} on the aluminum content can occur for ternary semiconductors like AlGaN (Ref. 12).

In this letter, we establish an experimental technique to determine the VB spacings in the UV spectral region. The idea is to use photoluminescence excitation (PLE) spectroscopy with the excitation light having an oblique angle of incidence. Because there is a lack of bright tunable light sources in the far UV, we performed our experiments using synchrotron radiation.

Two films both deposited by metal organic vapour phase epitaxy were investigated. The ≈470 nm thick AlN layer was grown at 920° on SiC. A Raman study performed at room temperature revealed small biaxial tensile strain of $\epsilon_{zz} = -5 \times 10^{-4}$ by analyzing the position of the E_2^{high} mode (for details of the strain determination technique see Ref. 13). The AlGaN layer was grown at 1200°C on c-plane sapphire. This layer is about 140 nm thick and placed on top of an AlN:O nucleation with about 20 nm thickness. The layer is

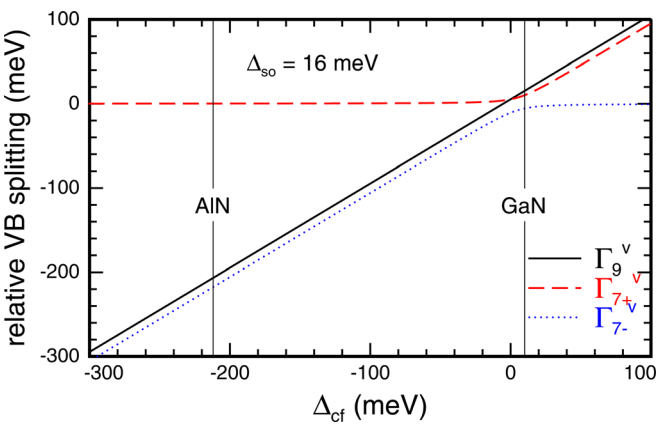

FIG. 1. (Color online) Relative valence band distances of wurtzite III-nitrides as a function of the crystal field splitting Δ_{cf}. The spin-orbit splitting was assumed to be constant (here, $\Delta_{so} = 16$ meV).

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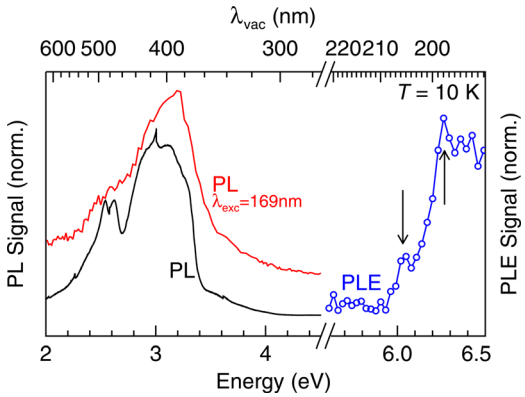

FIG. 2. (Color online) Comparison of photoluminescence spectra from the AlN sample excited by ArF* laser light (black, bottom line) and synchrotron radiation having $\lambda = 169$ nm (red, top line). The corresponding photoluminescence excitation spectrum (blue, open circles) shows two steps which are marked by arrows. All curves are recorded at $T = 10$ K.

c-oriented and has an aluminum content of about 94% as derived from high resolution x-ray diffractometry. Room temperature lattice constants of $a = 3.103$ Å and $c = 5.004$ Å indicate compressive in-plane strain[14] of $\epsilon_{xx} = -4.4 \times 10^{-3}$ and an out-of-plane strain of $\epsilon_{zz} = 2.3 \times 10^{-3}$.

Conventional photoluminescence (PL) studied for comparison was excited by an ArF* excimer laser ($\lambda = 193$ nm) under low excitation density conditions. The samples were placed in a cryostat allowing for experiments at 10 K. The emitted light was dispersed and recorded by a grating monochromator with attached charge-coupled device camera. Synchrotron-based PL and PLE experiments were performed using the light source DORIS III at DESY, Hamburg (Germany) on the Superlumi station at beamline I which is described in detail in Ref. 15 and references therein. The sample surface normal was oriented with $\approx 35°$ tilt relative to the excitation light beam, while the electric field vector of the incident light was polarized in the plane of incidence (p-polarized) ensuring that a certain fraction of light fulfills $\mathbf{E} \parallel c$ (required for studying $\Gamma_{7+}^{v} \rightarrow \Gamma_{9}^{c}$ transitions). The excitation energy resolution was about 10 meV at 6 eV. The emitted light was detected by a photomultiplier tube mounted to a grating monochromator. The center of the spectral detection window was set to the weak unstructured defect related emission around 3.73 eV for AlGaN and 3.18 eV for AlN. Additionally, for the AlGaN sample, spectroscopic ellipsometry (SE) measurements in steps of about 1 meV at 10 K under an angle of incidence of 67.5° were performed by a rotating-analyzer ellipsometer located at the synchrotron radiation source BESSY II, Berlin (Germany). For more details see Ref. 16.

In a first step, we compare the PL spectra of AlN excited either by ArF* laser light or by synchrotron radiation at $\lambda = 169$ nm. Both excitation sources yield the same broad luminescence peaking at around 3.18 eV (Fig. 2). No near-band-gap luminescence was detected for this specific sample using both setups. Tracking the emitted intensity at the peak energy of the detected recombination band while changing the energy of exciting photons, we recorded a PLE spectrum from the AlN sample, shown in Fig. 2 on the right hand side. From low to high energy, the PLE intensity shows two clear thresholds. We associate these two resonance energies at 6.03 ± 0.01 eV and 6.27 ± 0.01 eV with free excitons formed either with holes from the highest VB (Γ_{7+}^{v}) or the other two lower VBs, respectively. These lower valence subbands are too closely spaced to separate their contributions here. The detected peak splitting of 240 meV represents the energy difference between Γ_{7+}^{v} and Γ_{9}^{v} of bulk AlN under weak strain.[2] Using the room temperature strain value for estimating Δ_{cf}, we obtain −225 meV. This is in remarkable good agreement to the published values for strain free material.[2,3]

We now look on the $Al_{0.94}Ga_{0.06}N$ layer. Theoretically, we expect the exciton transition related to the Γ_{9}^{v} VB at 6.03 eV (for 10 K) using a bowing factor of $b = 0.9$ eV (Ref. 9). The PL spectrum of the AlGaN sample shows a broad unstructured defect band centered at 3.73 eV (not shown) and a contribution peaking at 5.78 eV (Fig. 3(c)). As the low energy emission is about 10× stronger than the near band gap signal under synchrotron radiation illumination, the former was chosen for recording PLE. Again, we find two steps in the PLE spectrum (Fig. 3(c)). The absorption onset energies are read from the trace as 5.87 ± 0.01 eV and 6.04 ± 0.01 eV, respectively. As clear excitonic peaks are absent in the PLE spectrum, these steps in absorption are assigned to a combination of broadened exciton, exciton continuum, and exciton-phonon interaction of the respective bands.[2] Excitonic resonances are possibly smeared out due to strong influence of polarization fields in the thin sample.[17]

The interpretation of the PLE onsets is confirmed by the results of SE, yielding the ordinary ($\mathbf{E} \perp c$) and extraordinary ($\mathbf{E} \parallel \mathbf{c}$) dielectric functions (DFs) by the approach reported

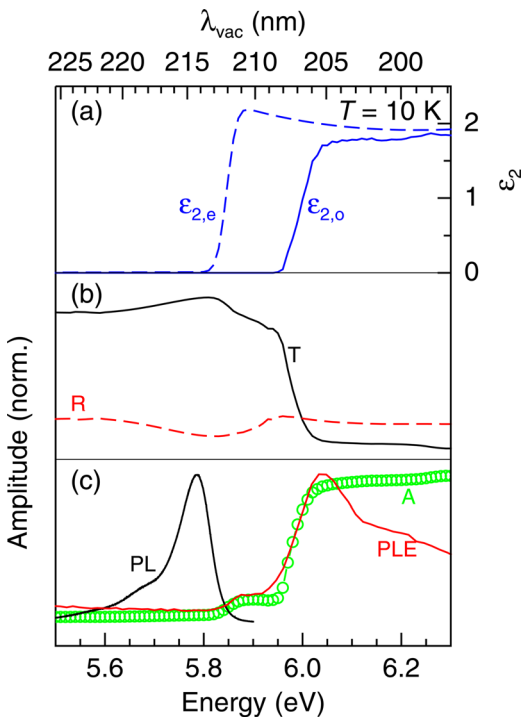

FIG. 3. (Color online) Results from the AlGaN sample at $T = 10$ K. (a) Imaginary parts of the ordinary ($\epsilon_{2,o}$) and extraordinary ($\epsilon_{2,e}$) dielectric function. (b) Calculated reflectivity (dashed line, red, R) and transmission (black, T) for p-polarized light with angle of incidence of 35°. (c) Comparison of photoluminescence excited by ArF* laser light (continuous line, black, PL) and the corresponding photoluminescence excitation spectrum (red, PLE). The calculated absorption is shown overlayed (open circles, green, A).

elsewhere.[2,18] Their imaginary parts $\epsilon_{2,o}$ and $\epsilon_{2,e}$ are displayed in Fig. 3(a). In contrast to the results for AlN,[2] no sharp excitonic resonances appear but merely step-like absorption edges. Using both DFs as starting point, we calculated transmission (T) and reflectivity (R) of the sample employing the conditions of the PLE experiment. Results are shown in Fig. 3(b). As only absorbed photons can contribute to the PLE signal, we compute the absorption ($A = 1 - R - T$) and compare it to the PLE spectrum in Fig. 3(c) showing a nearly identical line shape. Therefore, the steps in the PLE spectrum can be identified by transitions from the different VBs to the CB as in the case of AlN. This means that the near band edge peak of the PL band is found at ≈ 90 meV lower energy than the free exciton involving the Γ^v_{7+} VB, being the signature of exciton localization in the ternary alloy.[19] Exciton localization is confirmed by temperature dependent PL studies to be discussed in a forthcoming article. The combined Γ^v_9/Γ^v_{7-} to CB transition at 6.04 eV is in good agreement with our expectation. The energy distance to Γ^v_{7+} amounts to 170 meV. Calculation of Δ_{cf} is again complicated by the fact that the strain is determined at room temperature only. Assuming the same value for low temperature, we estimate $\Delta_{cf} = -220$ meV for $Al_{0.94}Ga_{0.06}N$.

Note that we see a decrease in the PLE spectrum for energies above 6.04 eV which is not represented by the absorption curve. This demonstrates that PLE is a more complicated process than absorption because relaxation of generated electron-hole pairs and their capture by radiative or nonradiative transitions plays a role as well.

Summarizing our letter, synchrotron based PLE is a versatile tool for investigating the valence band structure of III-nitrides in the far UV. We estimate crystal field splittings of $\Delta_{cf} = -225$ meV for AlN and -220 meV for $Al_{0.94}Ga_{0.06}N$. On the latter sample, we confirmed our interpretation independently by comparing PLE to the DF obtained by synchrotron spectroscopic ellipsometry. Obviously, PL spectra alone would yield a misleading value for the band edge energies. Synchrotron-based PLE will become particular important to study thin layers or materials with low absorption edge splittings where SE is not sensitive enough to distinguish between both DFs.

A part of this research was carried out at the light source DORIS III at DESY. DESY is a member of the Helmholtz Association (HGF). We would like to thank A. Kotlov for excellent assistance in using beamline I at DESY. Furthermore, we gratefully acknowledge support by the synchrotron radiation source BESSY II of the Helmholtz-Zentrum Berlin (HZB). We thank the groups of Y. Taniyasu, NTT (Japan) and F. Scholz, University of Ulm (Germany) for the AlN and AlGaN samples, respectively.

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