Electronic structure of GaN measured using soft-x-ray emission and absorption

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The electronic structure of thin-film wurtzite GaN has been studied using a combination of soft-x-ray absorption and emission spectroscopies. We have measured the elementally and orbitally resolved GaN valence *and* conduction bands by recording Ga L and N K spectra. We compare the x-ray spectra to the partial density of states from a recent *ab initio* calculation and find good overall agreement. The x-ray emission spectra confirm that the top of the valence band is dominated by N $2p$ states whereas they reveal that there is only weak hybridization between Ga $4s$ and N $2p$ states. Surprisingly, we found a weak feature in the N K emission at approximately 19.5 eV below the valence-band maximum that arises from hybridization between N $2p$ and Ga $3d$ states. X-ray absorption spectra show that the bottom of the conduction band is a mixture of Ga $4s$ and N $2p$ states, again in very good agreement with the theory. [S0163-1829(96)51348-7]

Refractory III-V nitrides (such as GaN, InN, and AlN) are an important class of wide-band-gap semiconductors, with possible use in optoelectronic, high-power and high-temperature devices.[1,2] Recent advances in growth techniques have enabled the production of high-quality single crystal GaN films on a variety of substrates.[1–3] Surprisingly, there is a dearth of experimental data concerning the basic electronic structure of such films, and this lack of knowledge inhibits their full technological exploitation. We present here the results of a soft-x-ray absorption (SXA) spectroscopy and soft-x-ray emission (SXE) spectroscopy study of the electronic structure of wurtzite (hexagonal) GaN thin films. SXE and SXA allow the occupied and unoccupied partial density of states of GaN to be measured directly, and the results are compared to a recent electronic structure calculation.[4] Our results show that the bottom of the valence band is primarily Ga derived, the top of the valence band is primarily of N $2p$ character, and the bottom of the conduction band contains both N and Ga contributions. We also have obtained evidence for weak hybridization between N $2p$ valence states and Ga $3d$ shallow core state. The agreement with the theory is quite good over a wide range of energies.

SXA and SXE are powerful probes of solid-state electronic structure, and are partially suitable for studying thin films of wide-band-gap semiconductors. Photon emission or absorption necessarily involves an optical transition between electronic states of the solid, and in the soft-x-ray regime one of the states is a localized dispersionless core level. This allows the interpretation of the measured spectra in terms of the density of unoccupied states for absorption, or occupied states for emission.[5–7] However, since dipole selection rules govern the transition to or from the core level, it is the angular-momentum-resolved density of states, or partial density of states (PDOS) that is in fact measured. Furthermore, since the core level is associated with a specific element in a compound, these spectroscopies are also elementally specific. They also have the advantage of being quite insensitive to the quality of the sample surface. This is not the case for photoemission spectroscopy (PES). While photoemission has recently been used to study well-characterized films of both hexagonal and cubic GaN,[8–11] it is inherently surface sensitive.[12,13] The bulk electronic structure can be measured (for occupied valence-band states) only if great care is taken to prepare and maintain atomically clean, stoichiometric, and ordered surfaces.[14] (Information of unoccupied states can also be extracted in principal, but requires fairly detailed knowledge of the matrix elements coupling the initial and final states in the photoemission process.)

The wurtzite GaN(001) thin films used in our experiments were grown using electron cyclotron resonance assisted molecular beam epitaxy on sapphire substrates; the growth procedure has been reported elsewhere.[3] The thickness of the samples was 0.54×10^{-6} m (as determined by scanning electron microscopy). The samples were auto doped n type, probably due to N vacancies, and had a resistivity of 2.8×10^{-3} Ω cm, a mobility of 37 cm^2/V sec and a high carrier concentration of 5.7×10^{19} cm^{-3}. Photoluminescence studies showed no evidence of deep-level yellow luminescence, further indicating high-quality films. SXA and SXE measurements were performed at the HASYLAB synchrotron facility, DESY, Hamburg, using the undulator beamline BW3, which is equipped with a modified SX-700 monochromator.[15] Absorption spectra were recorded in the total electron yield mode by measuring the sample drain current and were taken with energy resolutions of 0.13 eV at 400 eV (in the vicinity of the N $1s$ edge) and 1.0 eV at 1000.0 eV (in the vicinity of the Ga $2p$ edge), both corresponding to setting the monochromator's exit slit width to 80 μm. Since the soft-x-ray emission (fluorescence) process is weak compared to the competing nonradiative deexcitation channels, the

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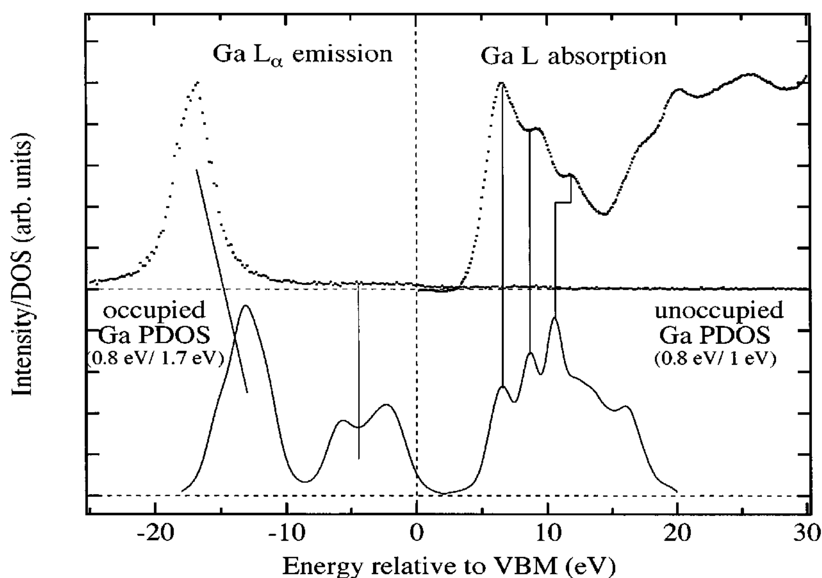

FIG. 1. Comparison of experimental Ga L spectra (upper panel) and partial density of states from Ref. 4 (lower panel). The energy values in parentheses are the full width at half maximum of the applied convolution function that simulate the effect of valence-hole lifetime and instrumental broadening, respectively (Lorentzian/Gaussian). Note that the empty and filled DOS are scaled separately. The energy scale is relative to the valence-band maximum (VBM). See text for details.

need for reasonable counting statistics required the use of a large exit slit width (400 μm, corresponding to an incident photon energy resolution of about 1 eV) during emission experiments. Emission spectra were recorded using a high-resolution grazing-incidence grating spectrometer.[16] The acquisition time for individual SXE spectra was approximately 30–60 min. When measuring emission to the N $1s$ core (at approximately 400 eV), the spectrometer used first order diffraction, while for emission to the Ga $2p$ core (at approximately 1000 eV) the spectrometer used second order diffraction at 15–20 μm entrance slit widths. A 5-m spherical grating with 1200 lines/mm was used for wavelength dispersion resulting in resolutions of 1.1 eV at 400.0 eV and 1.7 eV at 1000 eV. The base pressure in the experimental system was 1.0×10^{-8} Torr. This vacuum is quite adequate since both SXA and SXE are primarily bulk probes, and surface phenomena were not under investigation.

We report here soft-x-ray emission and absorption spectra of GaN and compare them with the *partial* density of states taken from Ref. 4. The spectra result from the following electronic transitions: $\{3d, 4s\}\rightarrow 2p_{3/2}$ (Ga $L\alpha$ emission), $2p_{3/2}\rightarrow\{3d, 4s\}$ (Ga L absorption), $2p\rightarrow 1s$ (N $K\alpha$ emission), and $1s\rightarrow 2p$ (N K absorption). Since the final state in x-ray emission contains a hole in the valence band rather than a hole in a core level, one expects that soft-x-ray *emission* spectra reflect the ground-state density of states (DOS) if the final-state rule is valid.[17] The final-state rule states that the spectral features that appear in x-ray spectroscopy correspond to the theoretical DOS calculated with the final-state potential. In general, x-ray *absorption* can only be compared to calculations that take into account core-hole effects but in favorable cases the resulting distortions are small.[18]

Since the results of two different measuring techniques will be compared, the procedures used for setting a common binding energy scale must be discussed. The x-ray spectrometer has a photon-counting position-sensitive detector, and the emission spectrum is obtained in the form of counts in an array of 1024 channels. In order to link the channel numbers to specific wavelengths (or photon energies) we use the following two procedures. For the N K spectra we use the diffuse elastic scattering of the incident photon beam, since this was strong enough to be clearly visible as a peak in the emission spectra. This allows us to associate a channel number with a photon energy, assuming that the monochromator calibration is correct.[19] We then recorded spectra at a number of different excitation energies and made a linear extrapolation to lower energies. This allows us to plot the SXE spectrum as a function of photon energy, i.e., the emission spectrum is plotted on the same energy scale as the absorption spectrum. Unfortunately, for Ga L emission, the diffuse scattering was too weak to be useful and we instead recorded the emission at higher photon energies where a second emission peak is visible, i.e., the $L\beta$-emission peak from $\{3d, 4s\}\rightarrow 2p_{1/2}$ transitions. The separation of these two peaks is just the spin-orbit splitting, which is 26.9 eV for GaN,[11] and hence the x-ray emission spectrum may be energy calibrated accordingly.

To put the emission and absorption spectra on a *binding energy* scale (as opposed to a photon-energy scale) we shifted the nitrogen SXE and SXA spectra rigidly until the high-energy cutoff of the SXE spectrum coincided with the valence-band maximum (VBM) from the theoretical N partial DOS.[20] Similarly, we adjusted the Ga SXE and SXA spectra (separately) so that the Ga gap as derived from theoretical calculations is reproduced. There is thus more uncertainty in the energy scale of the Ga L spectra than for the N K spectra.

In Fig. 1 we display the Ga L emission and absorption spectra (upper panel) and compare them to the Ga-projected DOS of Ref. 4 (lower panel). As indicated in Fig. 4, we first convoluted the theoretical DOS by Lorentzians to simulate $2p_{3/2}$ core-hole lifetime broadening and then convoluted the theoretical DOS by Gaussians to simulate the instrumental broadening. The prominent peak in the $L\alpha$-emission spectrum reflects the Ga $3d$ states in GaN at about 17 eV below the valence-band maximum (VBM). We attribute the long, weak emission band that extends up to the top of the valence band to Ga $4s$ states. Both features find their correspondence in the DOS, which is indicated by the lines between the panels. The relatively small intensity ratio of the Ga $4s$ to Ga $3d$ emission perhaps indicates some overestimation of the Ga $4s$-N $2p$ hybridization in the theoretical DOS calcula-

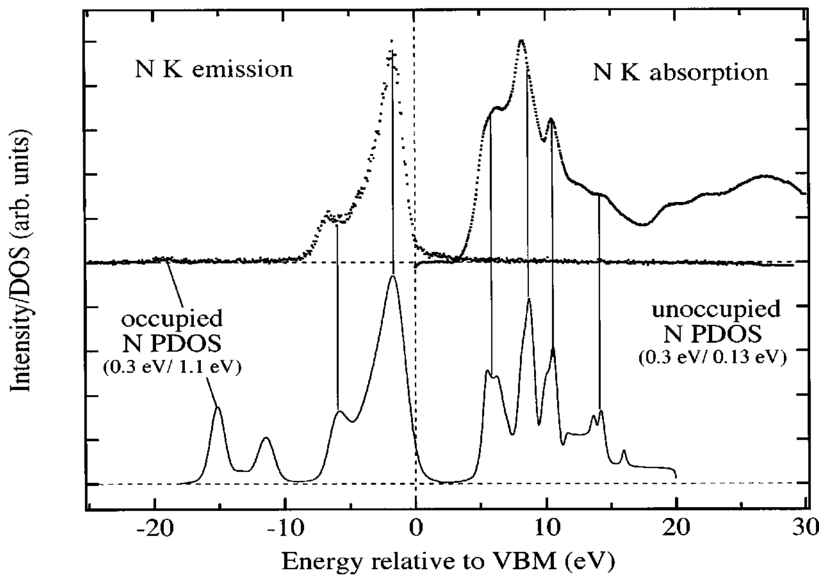

FIG. 2. Comparison of experimental N K spectra (upper panel) and partial density of states from Ref. 4 (lower panel). See Fig. 1 caption for further details.

tion, even considering differences in s-to-p and d-to-p transition probabilities. The discrepancy between the energy positions of the Ga $3d$ states in the theoretical DOS and the x-ray emission spectrum in an analogue to the case in photoemission spectroscopy (PES) and has already been investigated earlier.[8] We note that the binding-energy position of Ga $L\alpha$ emission and the corresponding Ga $2p$ photoemission peak are in good agreement, but that the width of the Ga $L\alpha$ peak is much larger.[8] This is due to the combination of the $2p_{3/2}$ core-hole lifetime and additional final-state phonon broadening (both about 0.8 eV) and the instrumental resolution of the x-ray emission spectrometer (1.7 eV at 1000 eV). Considering the absorption data in Fig. 1, we also see a clear correspondence between the spectral features of the Ga L absorption and the unoccupied partial DO8, indicated by the lines between the panels. However, the farther from the bottom of the conduction band the larger the energy shift of the peaks.

Figure 2 is a similar comparison between the N x-ray spectra and the occupied and unoccupied N-projected states. In N $K\alpha$ emission we observe an approximately 7-eV-wide N $2p$-like band forming the top of the valence band, in accord with theory.[4] The DOS in this range has also been measured by PES, but this method does not provide information on the elemental character of the band.[8] Note that a shoulder is visible in the photoemission spectra just above the energy of the Ga $3d$ states that originates from N $2s$ states (see Ref. 8), but due to the dipole selection rules such features cannot appear in N K emission. It may be possible, however, to see the effect of hybridization of the N $2s$ and the Ga $3d$ in the $L\alpha$ emission by using even higher resolution in future. A very weak feature that appears at about 19.5 eV below the top of the valence band may be related to N $2p$–Ga $3d$-hybridization bands. Considering the absorption data in Fig. 2, we note that K absorption involves a core hole without angular momentum. This reduces complications from spin-orbit coupling and hence often results in spectra that reflect the empty DOS more directly then, for example, in L absorption.[18] As evident in Fig. 2 this seems to be the case for N K absorption of GaN since we find very good agreement between the spectral features and the features in DOS.

In Fig. 3 we display the tail contributions of Ga $L\alpha$ and N K emission on an enlarged vertical scale. The bottom curve shows the partial DOS again from Ref. 4. The heavy lines are three-point binomially smoothed versions of the corresponding x-ray emission spectra. In N K emission we clearly see a peak that rises above the background at -19.5 eV. We tentatively attribute this to the lowest-energy peak seen in the N partial DOS. Since dipole selection rules are very stringent in this energy regime, this peak must originate from a N $2p$ contribution that probably arises due to hybridization with Ga $3d$ states which are close in energy. The Ga $4s$ states that are reflected in the tail of Ga $L\alpha$ extend to the top of the

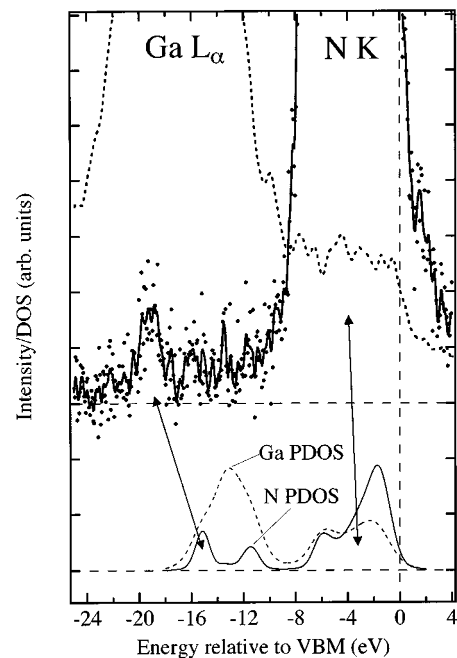

FIG. 3. Upper panel: Raw data of N K emission (dots), three-point binomially smoothed Ga $L\alpha$ emission (dashed heavy line) and N K emission (solid heavy line) on elongated vertical scale. Lower panel: broadened theoretical partial density of states from Ref. 4 (solid line, N partial DOS; dashed line, Ga partial DOS).

valence band. In contrast to theory (bottom curve) no clear gap separates them from the Ga $3d$ states.

We also investigated the variation of the x-ray emission spectra with excitation energy by tuning the incident energy from close to the absorption edges to far above, but we observed little change in the structure of the spectra. This result is somewhat surprising considering recent x-ray emission measurements on certain other systems that showed strong dispersionlike effects which were explained in the inelastic scattering picture.[21] Also angle resolved photoemission studies of GaN reveal strong band dispersion for the valence band.[11,22] However, the spread in energy of the incident monochromatic photon beam determines the size of the contributing region in the Brillouin zone and therefore it may be necessary to use much better resolution than applied in this work to see dispersion effects in x-ray emission of GaN.

In conclusion, we have presented a detailed study of the electronic structure of GaN using x-ray emission and absorption spectroscopy. From the spectra we have determined the elementally and orbitally resolved character within the valence and conductance bands and we have confirmed the validity of the final-state rule in x-ray emission for wide-band semiconductors. There is good overall agreement between the calculated DOS and the experimental spectra although discrepancies regarding energy positions and hybridization strengths remain.

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[19] The accuracy of this method depends on the combined instrumental resolution of the monochromator and the spectrometer as well as on the relative visibility (number of counts) of the elastic peak. The monochromator calibration is accurate to within 5%, and since we are using relative energy differences in the spectra, we use the monochromator setting as the photon energy. Clearly the *absolute* energy scale, which is not of primary interest here, is less accurate.

[20] Another method for establishing a binding-energy scale is to subtract the binding energy of the core levels, i.e., N $1s$ and Ga $2p_{3/2}$ in GaN as measured by PES, for instance. For this one needs a very accurate knowledge of the absolute x-ray energies and core-level energies but this was not readily available to us.

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