Measuring electronic structure of wurtzite InN using electron energy loss spectroscopy

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The electronic structure of wurtzite InN has been investigated by electron energy loss spectroscopy (EELS). Spectra of the nitrogen K edge and the indium $M_{4,5}$ edge have been measured and were compared with calculated partial, N $2p$ and In $5p$ conduction band density of states in InN. Excellent agreement on the relative positions of the characteristic peaks were obtained. From low-loss EELS the bulk plasmon energy at 15.5 eV, location of the In $4d$ deep valence states at about 16.3 eV below the conduction band maximum and strong interband transitions with 6.2 eV excitation energy are also found. © *2003 American Institute of Physics.*
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Recent successes in the growth of high quality wurtzite InN[1–3] have resulted in substantial interest in the use of InN in the fabrication of high performance high electron mobility transistors and light-emitting diodes.[4] This has generated a need for reliable data for the basic structural, electronic, and optical parameters and properties for InN. However, only a few measurements of electronic states, using x-ray absorption,[5,6] have been reported. Electron energy loss spectroscopy (EELS) is another effective technique to probe these basic electronic and optical properties. For example, the intimate connection between local densities of the unoccupied electronic states (LDOS) and the core-level excitation spectra[7] allows a measurement of the energy distribution and densities of states for the levels above Fermi energy. The low-loss region of EELS contains information on optical properties, such as electronic transitions between critical points of conduction and valence bands, which give rise to characteristic peaks with corresponding energies, and the plasmon-loss energy, which can be used as an ultimate test for real part of dielectric function known to satisfy $\mathrm{Re}[\varepsilon(\omega)]=0$ at $\omega=\omega_p$.[8]

However, to assess the reliability of measured data, strong correlation between calculated and measured values is essential. In this letter we report a comparison of theoretical density-of-states calculations with EELS measurements of the nitrogen K edge, indium $M_{4,5}$ edge, and low energy-loss spectra on wurtzite InN.

The wurtzite form of InN studied here was grown by conventional molecular beam epitaxy on a sapphire substrate with 200 nm AlN buffer layer.[3] The measured Hall mobility of the quasi two dimensional electron gas in this sample was about 1200 $\mathrm{cm}^2/\mathrm{V\,s}$ with a sheet carrier concentration of 1.2×10^{14} cm^{-2}. Plan-view samples were prepared for scanning transmission electron microscopy (STEM) from this wafer by tripod polishing.[9] Details on the Cornell 100 kV UHV VG HB501 STEM used for these measurements can be found elsewhere.[7]

As a first step in understanding the nature and rate of the electron beam induced damage in InN occurring during observation in STEM, measurements of the damage in the sample were carried out. Expulsion of nitrogen from samples (leaving behind metallic In) was observed. For these samples we found that the spectra do not show any detectable damage until at least 10 s of acquisition time with a beam current of about 8.5×10^{-2} nA. A long acquisition time is needed to obtain low noise EELS data and, therefore, in all further core-level EELS measurements we used 10 s as the upper limit for spectrum acquisition time.

The spectra of core-level EELS with its fine structure are highly correlated with the appropriate local density-of-states at the site of the excited atom.[7] Comparison of our core-loss EELS data with corresponding calculated LDOS provides a good test of the calculations and confirms details of the electronic structure of InN. For that reason tens of N K-edge and In $M_{4,5}$-edge spectra were obtained. After background subtraction, all spectra were compared in order to reveal the consistency of the major features and then were added to reduce noise.

The excitations of the N $1s$ core-level electrons to the empty N $2p$ states of the conduction band give rise to the characteristic N K-edge spectrum in EELS as shown in Fig. 1 where the positions of prominent peaks are identified. The dashed line in the same figure is the calculated N $2p$ partial density of states in the conduction band of the InN. Calculations of the LDOS were carried out using the density functional theory (DFT) within the local density approximation.[10] The implementation of the DFT is through the Vienna *Ab initio* Simulation Package[11] (VASP), which uses a plane-wave basis set, along with Vanderbilt ultrasoft pseudopotentials.[12] The calculated LDOS curve presented

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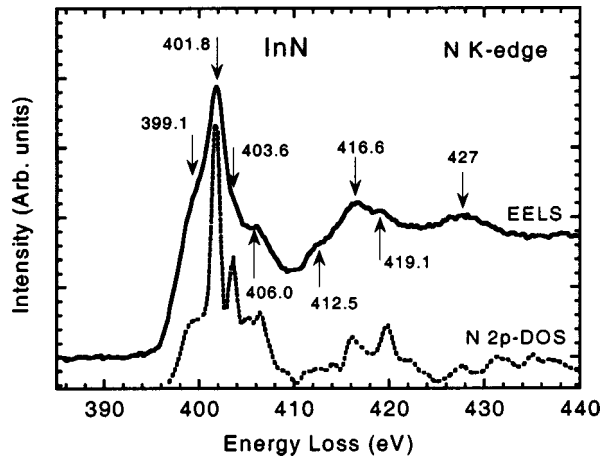

FIG. 1. Nitrogen *K* edge from EELS measurements in wurtzite InN (solid line) with calculated nitrogen N $2p$ partial DOS (dashed line). To eliminate small energy drift in STEM the spectrum is aligned with corresponding x-ray absorption data (Ref. 5). The DOS calculations are aligned to EELS by displacing the primary peak to 401.8 eV for better comparison of the remaining features.

here is aligned to the sharp peak at 401.8 eV. All the major peaks predicted by calculations are observed in EELS measurements, and there is excellent agreement in the relative position of the peaks. Strictly speaking, the peaks in the continuum ($>\sim 410$ eV) reflect resonant inelastic scattering enhancement of the free particle states. X-ray absorption measurements[5] performed on InN also confirm the presence of most of the peaks of the N *K* edge observed in our EELS. The peak at 419.1 eV observed in EELS measurements and predicted by calculations has not been seen earlier.

Unlike the N *K* edge, the spectrum of the In $M_{4,5}$ edge does not exhibit strong fine structure. In general the $M_{4,5}$ edge arises from electronic transitions from $3d$ core-level states to the corresponding dipole projected $k^{\mathrm{cond}}p$ or $k^{\mathrm{cond}}f$ empty conduction band states. These $l \rightarrow l \pm 1$ transitions are governed by the dipole selection rule. However, the matrix elements for these transitions exhibit a delayed maximum which impacts the EELS spectrum of the $M_{4,5}$ edge. In indium, the $3d$ core-level states are less strongly localized[13] than, for example, typical *s* states and therefore, all energy-loss spectra with transitions from these states should contain the features with at least the same full width at half maximum as $3d$ states. All of these contribute to the characteristic core-level EELS of the $M_{4,5}$ edge in InN presented in Fig. 2(a). Three broad peaks, P_1, P_2, and P_3 at about 472, 479, and 488–490 eV, however, still can be identified. The results of x-ray photoemission spectroscopy measurements[14,15] suggest that the primary contributions to the In $M_{4,5}$ edge in EELS come from transitions of the electrons from the In $3d_{3/2}$ and $3d_{5/2}$ states (according to these measurements they are separated by 7.6 eV) to corresponding In $5p$ empty states of the conduction band (transitions to energetically higher located In $4f$ states were neglected here and these $4f$ states have also not been taken into account in calculations). To illustrate this, we convolved the spectrum of the In $3d_{3/2}$ and $3d_{5/2}$ states [Fig. 2(b)] with a calculated partial, In $5p$, conduction band LDOS [Fig. 2(c)]. The result is presented in Fig. 2(a) (dashed curve). As is seen, this simple model explains the presence of peaks P_1–P_3 in our EELS measurements.

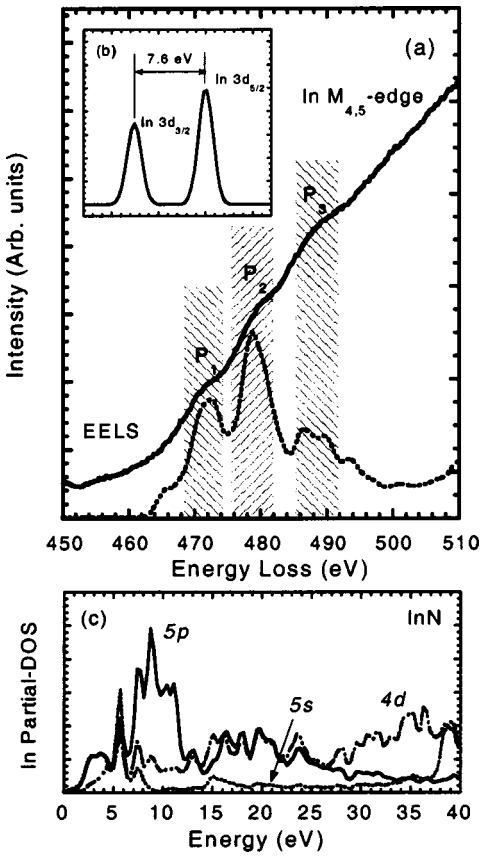

FIG. 2. (a) In $M_{4,5}$ edge from EELS measurements in wurtzite InN (solid line) with its theoretical prediction (dashed line) obtained by convoluting In $3d_{3/2}$ and $3d_{5/2}$ states (from Refs. 14 and 15) and (b) with corresponding In $5p$ empty conduction band DOS. (c) Partial, In $5s$, $5p$, and $4d$, DOS of the conduction band.

The next step was the study of the low-loss region of the EELS in InN. Tens of low-loss spectra were again collected and compared to check consistency of their major features, and several of them were combined to reduce noise. Then standard Fourier–Log deconvolution[16] was applied to remove multiple inelastic scattering, including strong multiple plasmon excitations. The resulting single inelastic scattering distribution (SSD) is presented in Fig. 3. The strong peak located at 15.5 ± 0.1 eV is identified as the plasmon-loss which is normally the main feature of the low-loss region. The peak IB at 6.2 ± 0.1 eV is believed to be due to strong electronic interband excitations between Van Hove critical points of the valence and conduction bands. If this is the case, then the corresponding peak should exist in the imaginary part of the dielectric function. And indeed first-principles calculations of the dielectric function for the wurtzite InN with quasiparticle corrections (for the band gap) reported by Persson *et al.*[17] indicate the presence of a strong peak at 5.8–7.0 eV in the imaginary part of the dielectric function.

Band structure calculations, as in the case of GaN, indicate the presence of well-defined In $4d$ deep valence states in the InN. In low-loss EELS, electrons in these In $4d$ states undergo transitions into dipole projected unoccupied conduction band *p* states. A calculated In $5p$ partial LDOS of the conduction band convoluted with a simple Gaussian function

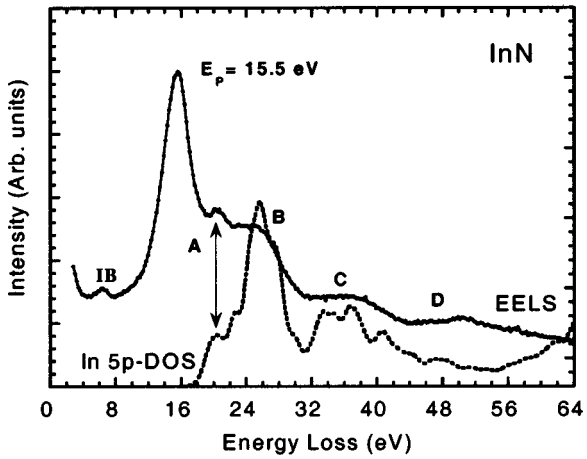

FIG. 3. Single scattering distribution obtained from low-loss EELS. The dashed line is calculated In $5p$ partial DOS of the conduction band convoluted with In $4d$ valence states.

(approximated for $4d$ states) is also presented in Fig. 3 (dashed line). The first peak of the LDOS curve is aligned with peak A at 20.4 ± 0.1 eV. As can be seen it describes the existence of peaks A–C in low-loss EELS (the broad peaks B and C are located within 23–25 and 34–40 eV energy ranges, respectively). These transitions from In $4d$ deep valence states are very similar to those observed in GaN (with transitions from the Ga $3d$ localized valence states to the Ga $4p$ empty states of the conduction band).[18]

Our measurements coupled with calculations indicate that these highly localized In $4d$ deep valence band states in wurtzite InN are 16.3 ± 0.5 eV below the minimum of the conduction band. These results of EELS measurements can also be used to locate the energy levels of these "d" states relative to the valence band maximum, assuming that the band gap is known. Unlike GaN or AlN, there is a wide range of values for the band gap of InN in the literature ranging from 0.8 to 0.9 eV to 1.5 and extending up to 1.9 eV.[19–21] By adopting the latest measured value of band gap of about 0.8 eV[19,21] then the In $4d$ deep valence band states should be 15.5 ± 0.5 below the top of the valence. Photoelectron spectroscopy measurements[14] carried out in InN also indicates the existence of In $4d$ states in InN, with a strong peak of 15.9 eV below valance band maximum.

Although most of the peaks in the SSD are identified as part of the $4d\rightarrow5p$ transitions, theoretical DOS shows no corresponding states for broad peak D (at 48–52 eV), which suggests that it is not part of these $4d\rightarrow5p$ transitions. While the exact origin of the peak D is not clear, it is possible that peak D is due to energetically favorable In $4d\rightarrow4f$ transitions with a delayed maximum.[13] Since, as was mentioned earlier, these In $4f$ states have not been included in the present DOS calculations, direct quantitative comparison cannot be presented here.

In conclusion, EELS studies of wurtzite InN using a UHV STEM were carried out. The measured spectra of the nitrogen K edge and indium $M_{4,5}$ edge are in excellent agreement with calculated partial, N $2p$, and In $5p$ partial DOS of conduction band on the relative positions of major peaks. From low-loss EELS, the position of the bulk plasmon-loss peak at 15.5 eV and location of In $4d$ deep valence states, 16.3 ± 0.5 eV below the minimum of the conduction band, are obtained. Strong interband transitions with energy 6.2 eV are also observed. These results provide firm starting points for further calculations and measurements of optical and electronic properties of wurtzite InN, e.g., dielectric function, absorption coefficient, and refractive index.

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[1] V. Yu. Davydov, V. V. Emtsev, I. N. Goncharuk, A. N. Smirnov, V. D. Petrikov, V. V. Mamutin, V. A. Vekshin, S. V. Ivanov, M. B. Smirnov, and T. Inushima, Appl. Phys. Lett. **75**, 3297 (1999).
[2] E. Kurimoto, H. Hamira, A. Hashimoto, and A. Yamamoto, Phys. Status Solidi B **228**, 1 (2001).
[3] H. Lu, W. J. Schaff, J. Hwang, H. Wu, G. Koley, and L. F. Eastman, Appl. Phys. Lett. **79**, 1489 (2001).
[4] S. Strite and H. Morkoc, J. Vac. Sci. Technol. B **10**, 1237 (1992).
[5] K. Lawniczak-Jablonska, T. Suski, Z. Liliental-Weber, E. M. Gullikson, J. H. Underwood, R. C. C. Perera, and T. J. Drummond, Appl. Phys. Lett. **70**, 2711 (1997).
[6] K. Lawniczak-Jablonska, T. Suski, I. Gorczyca, N. E. Christensen, K. E. Attenkofer, R. C. C. Perera, E. M. Gullikson, J. H. Underwood, D. L. Ederer, and Z. Liliental-Weber, Phys. Rev. B **61**, 16623 (2000).
[7] D. A. Muller, D. J. Singh, and J. Silcox, Phys. Rev. B **57**, 8181 (1998).
[8] R. H. Ritchie, Phys. Rev. **106**, 874 (1957).
[9] J. P. Benedict, R. Anderson, S. J. Klepeis, and M. Chaker, Mater. Res. Soc. Symp. Proc. **199**, 189 (1990).
[10] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[11] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
[12] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[13] S. T. Manson and J. W. Cooper, Phys. Rev. **165**, 126 (1968).
[14] Q. X. Guo, M. Nishio, H. Ogawa, A. Wakahara, and A. Yoshida, Phys. Rev. B **58**, 15304 (1998).
[15] B. R. Natarajan, A. H. Eltoukhy, and J. E. Greene, Thin Solid Films **69**, 201 (1980).
[16] R. F. Egerton, *Electron Energy Loss Spectroscopy in the Electron Microscope* (Plenum, New York, 1996).
[17] C. Persson, R. Ahuja, A. Ferreira da Silva, and B. Johansson, J. Phys.: Condens. Matter **13**, 8945 (2001).
[18] K. A. Mkhoyan and J. Silcox (unpublished).
[19] V. Yu. Davydov, A. A. Klochikhin, R. P. Seisyan, V. V. Emtsev, S. V. Ivanov, F. Bechstedt, J. Furthmuller, H. Harima, A. V. Mudryi, J. Aderhold, O. Semchinova, and J. Graul, Phys. Status Solidi B **229**, R1 (2002).
[20] T. Inushima, V. V. Mamutin, V. A. Vekshin, S. V. Ivanov, T. Sakon, M. Motokawa, and S. Ohoya, J. Cryst. Growth **227–228**, 481 (2001).
[21] J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. Lu, W. J. Schaff, Y. Saito, and Y. Nanishi, Appl. Phys. Lett. **80**, 3967 (2002).