# Electronic structure of indium nitride studied by photoelectron spectroscopy

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Photoemission studies were carried out on indium nitride single crystals. The peaks for N $1s$, In $3d_{5/2}$, and In $3d_{3/2}$ were observed with binding energies of 396.0, 443.6, and 451.2 eV, respectively. We observed a valence band with width of 10 eV showing two distinguishable features at binding energy of 3.9 and 7.4 eV. Reasonable agreement for the valence-band width was found between the experimental data and the theoretical results calculated using empirical pseudopotential method. [S0163-1829(98)07047-7]

Indium nitride (InN) with a direct band gap of 1.9 eV, is a promising material for optoelectronic devices, low-cost solar cells with high efficiency, optical coatings, and various types of sensors.[1] Recently, it has received more attention from the properties of its alloys with GaN and AlN, which permit the fabrication of $In_xGa_{1-x}AlN$ based shortest-wavelength semiconductor laser diode.[2,3] Moreover, InN has distinct advantages in high-frequency centimeter and millimeter wave devices, because the transport characteristics of InN are superior to those of GaN as well as GaAs.[4] The potential of InN in such device applications is now further enhanced by the possibility of epitaxial growth of InN on various substrates such as sapphire,[5–7] GaAs,[8] and GaP.[8] A study of the electronic structure of this material is important not only for fundamental understanding of the material, but also for technological applications. Several calculations of band structure for InN have been reported.[9–12] Unfortunately, these theoretical results conflict each other, suggesting the need for experimental measurements to clarify the electronic structure of InN. It is well known that photoemission is a powerful method to investigate the electronic structure.[13] When data from a range of compounds containing the atom in question are compared, core electron binding energies show a chemical shift effect, which offers in principle a means of determining the distribution of valence electron density in compounds. Moreover, photoelectron energy distribution curve for the valence band is directly related to the calculated density of states in the valence band. However, a comprehensive photoemission study for InN has not been performed so far. In this paper, the core electron binding energies of indium and nitrogen in InN compound are investigated by conventional x-ray photoemission spectroscopy (XPS). Modern synchrotron radiation photoemission spectroscopy, which most contributed in the past few years to clarify the electronic band structure of solids,[14] is used to probe the electronic density of states and test the validity of existing theoretical band-structure calculations for InN.

InN films were grown on (0001) oriented sapphire ($\alpha$-$Al_2O_3$) substrates by microwave-excited metalorganic vapor phase epitaxy. Details of the growth method are described elsewhere.[5] To assess the crystallinity and crystallographic orientation of the obtained InN films, reflection high-energy electron diffraction (RHEED) and x-ray diffraction (XRD) patterns were taken. All of the samples used in the photoemission measurements exhibit sharp RHEED diffraction spots as shown in Fig. 1. The XRD patterns exclusively include peaks at the Bragg angles (0002) and (0004) in InN, and (0006) and (00012) in sapphire, i.e., the $\{000l\}$ group. These data certainly show that the (0001) InN films have been grown epitaxially on the (0001) sapphire substrate, and the $c$ axis of the InN crystal is aligned normal to the substrate surface. Visual inspection by an optical microscope showed that the films have a featureless, rather smooth surface. The film thickness measured with a surface profile analyzer was about 0.3 $\mu$m. Conventional x-ray photoemission data were collected using Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV). Synchrotron radiation photoemission spectroscopy measurements were performed using radiation from the 750-MeV electron storage ring of UVSOR at the Institute for Molecular Science.

Figure 2 shows a typical whole XPS spectrum from InN. The indium (In $3p_{1/2}$, In $3p_{3/2}$, In $3d_{3/2}$, In $3d_{5/2}$, In $4s$, In $4p$, and In $4d$) and nitrogen (N $1s$) peaks as well as carbon (C $1s$) and oxygen (O $1s$) peaks are observed. The carbon and oxygen peaks were not detected after sputter etching with an Ar-ion beam (4 kV, 10 $\mu$A) for 3 min. This clearly indicates that carbon and oxygen are the surface contaminants. Figure 3(a) and 3(b) show the In $3d$ and N $1s$ region XPS spectra, respectively. All the binding energies were corrected with contamination C $1s$ signal (284.6 eV). The obtained binding energies are 396.0, 443.6, and 451.2 eV for N

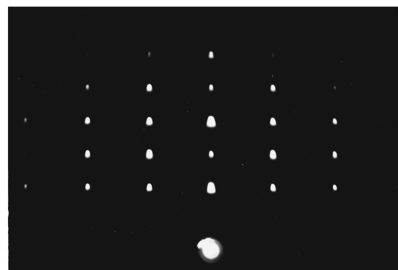

FIG. 1. A typical RHEED pattern of the InN thin films. The electron beam is parallel to the $[2\bar{1}\bar{1}0]$ azimuth of InN.

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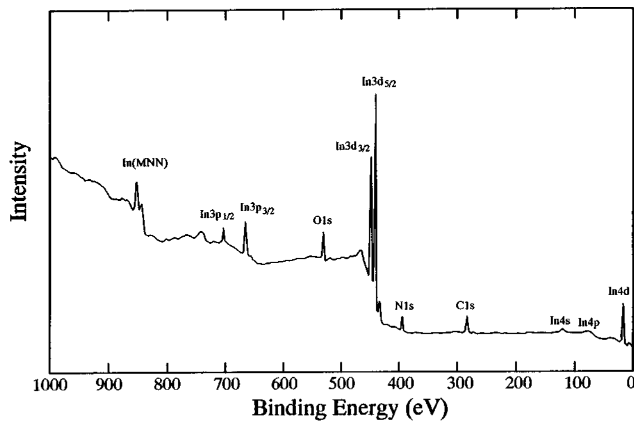


FIG. 2. X-ray photoelectron survey spectrum from InN using Mg $K\alpha$ radiation ($h\nu$=1253.6 eV).

$1s$, In $3d_{5/2}$, and In $3d_{3/2}$, respectively, which are of about 0.8 eV lower than those measured by Natarajan, Eltoukhy, and Greene[15] on sputter-deposited indium nitride. However, the separations in energy between the N $1s$, In $3d_{5/2}$, and In $3d_{3/2}$ are equivalent, although crystallinity of the samples are different: the samples used in the present study are single crystalline as shown in Fig. 1, and those of Natarajan, Eltoukhy, and Greene are polycrystalline.[15] Kovacich *et al.*[16] have investigated the chemistry of sputter-deposited AlN crystals with different crystallography by XPS. They found no difference in N $1s$ and Al $2p$ binding energies between the sample with a single basal orientation and the sample that is semiamorphous. Thus, we believe the discreprepancy for the absolute binding energies are not ascribed to the difference of crystallinity of the sample. Since x-rays striking the sample yield photoelectrons and these in turn can excite secondary electrons in x-ray photoemission, many of these electrons are sufficiently energetic to leave the sample at the surface from which photoelectrons are being analyzed.[17] This surface becomes positively charged until the photoelectron-plus-secondary current is counterbalanced by a neutralizing current origination from ground or from ambient space charge. The sample will be positively charged and the whole spectrum shifted to higher binding energies. Thus, it is necessary to make correction for static charge in order to identify the absolute binding energies accurately. The binding energy shift due to the charging effect was obtained to be 0.6 eV in the present study by comparing the observed binding energy of C $1s$ to its standard value. This indicates that our uncorrected binding energies of indium and nitrogen are almost equal to those of Natarajan, Eltoukhy, and Greene. Here, we note that no description on the energy calibration is given in the paper of Natarajan, Eltoukhy, and Greene.[15]

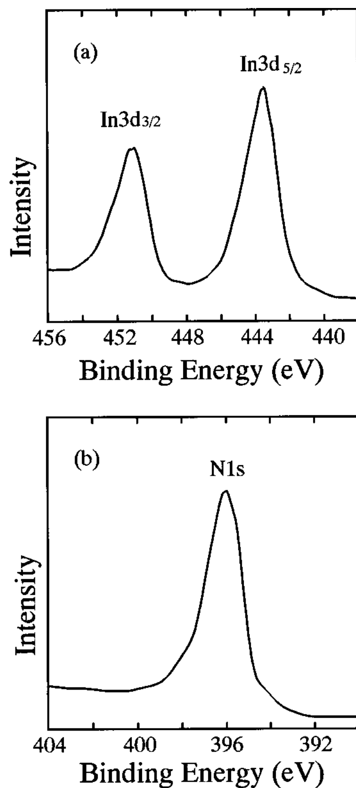


FIG. 3. (a) In $3d$ and (b) N $1s$ x-ray photoelection spectra from InN.

TABLE I. Nitrogen $1s$ binding energy for some III–V nitride compounds.

| Nitride compounds | N $1s$ binding energy (eV) | |
|---|---|---|
| InN | 396.0 | This work |
| $Al_{0.14}In_{0.86}N$ | 396.6 | Ref. 18 |
| AlN | 396.7 | Ref. 16 |
| BN | 397.8 | Ref. 19 |

Table I summarizes the binding energy of N $1s$ in some III-V nitrides. Clearly, the N $1s$ binding energy increases as the host cation is altered from In to Al to B. We hope these data will stimulate further theoretical studies on III-V nitride compounds.

In the lowest section of Fig. 4 we show a typical photoelectron spectrum of InN single crystals excited with syn-

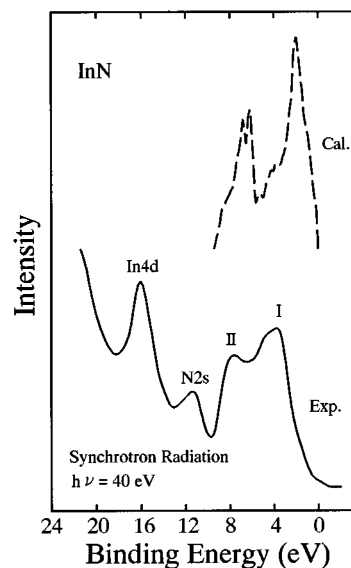


FIG. 4. Photoelectron spectra of InN excited with synchrotron radiation at photon energy of 40 eV. The broken line is the valence-band density of states for InN calculated by Foley and Tansley (Ref. 9) using emprical pseudopotential method.

chrotron radiation at photon energy of 40 eV. The peak observed at the binding energy of 15.9 eV is ascribed to the emission from In $4d$ states, which is also clearly observed in conventional XPS spectra as shown in Fig. 2. The peak appeared at the binding energy of 11.4 eV is believed to correspond to the N $2s$ electrons,[20] because the band structure is similar between the nitrides of aluminum, gallium, and indium,[11] like the more familiar III-V compounds such as the phosphides, arsenides, and antimonides of aluminum, gallium, and indium. The valence-band width for InN is estimated to be 10 eV and two distinguishable features labeled I and II occur at the binding energies of 3.9 and 7.4 eV, respectively. For InN, several theoretical calculations of the band structure have been carried out.[9–12] Foley and Tansley[9] used the empirical pseudopotential method (EPM) to calculate the band structure, density of states, and the imaginary part of the dielectric function. They obtained a valence-band width of 9.6 eV. Tsai *et al.*[10] predicted a valence-band width of 6.8 eV by using the pseudofunction method to selfconsistently solve the one electron Schrödinger equation in a local-density approximation. Christensen and Gorczyca[11] investigated the optical and structural properties of InN by means of the linear muffin-tin-orbital method in its scalar-relativistic form in conjunction with the local-density approximation (LMTO-LDA) to the density-functional theory, and gave a valence-band width of 5.7 eV. Recently, Yeo, Chong, and Li[12] calculated the band structure of InN by the EPM and obtained a valence-band width of 5.8 eV, which differs from the result of Foley and Tansley, however, has a good agreement with that calculated by LMTO-LDA method. The EPM calculation by Foley and Tansley is in good agreement with our experiment as far as the width of the valence band is concerned. For comparsion, the valence-band density of states for InN calculated by Foley and Tansley[9] is shown in the topmost section of Fig. 4. Reasonable agreement was obtained between the calculated and experimental results, although the positions of the features are different.

In conclusion, photoemission studies were carried out on indium nitride single crystals. The peaks for N $1s$, In $3d_{5/2}$, and In $3d_{3/2}$ were observed in the conventional x-ray photoelectron spectra with binding energies of 396.0, 443.6, and 451.2 eV, respectively. Synchrotron radiation photoemission spectroscopy was used to probe the electronic density of states and test the validity of existing band-structure calculations. A valence band with width of 10 eV showing two distinguishable features at binding energy of 3.9 and 7.4 eV was obtained. Reasonable agreement for the valence-band width was found between our experimental data and that calculated by Foley and Tansley using empirical pseudopotential method.

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