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Letter

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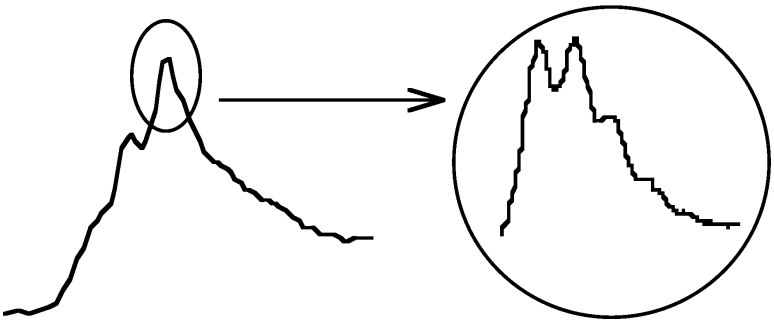

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Direct Observation of Defect Levels in InN by Soft X-ray Absorption Spectroscopy

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We have used synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to study the electronic structure of nitrogen-related defects in InN(0001). Several defect levels within the band gap or the conduction band of InN were clearly resolved in NEXAFS spectra around the nitrogen K-edge. We attribute the level observed at 0.3 eV below the conduction band minimum (CBM) to interstitial nitrogen, the level at 1.7 eV above the CBM to antisite nitrogen, and a sharp resonance at 3.2 eV above the CBM to molecular nitrogen, in full agreement with theoretical simulations.

Interest in InN has increased significantly during the past few years as rapid advances in thin film deposition techniques have led to much better quality samples,[1] leading to more consistent information on properties of InN and even the revision of its fundamental band gap energy from 1.9 eV to around 0.7 eV.[2] Although the band parameters of InN are still under debate,[3] the likelihood of a lower InN band gap energy has opened the possibility for a single material system, the ternary alloy InGaN, to span the band gap from the near-infrared (InN) to the ultraviolet (GaN). One obvious application of this exciting possibility is the conversion of the full spectrum of sunlight to electrical current by a single material system.

To fully realize the potential of InN, a fundamental understanding of point defects as well as surface and interface properties is required, as these may control some vital characteristics of nitride semiconductors, ranging from the type of conductivity to dopant diffusion. However, InN is the least studied of the group III nitrides, and there are almost no experimental reports on defects in InN. To our knowledge, the present work provides the first direct experimental observation of point defects and formation of molecular nitrogen in InN.

Several native defects, such as vacancies and antisites, have been identified and characterized previously only theoretically.[4,5] However, the theoretical study of defects in InN is confusing and incomplete. For example, no calculation for nitrogen or indium interstitial levels is provided in the literature, while the position of levels created by some other defects seems to be controversial.

In an early tight-binding calculation of the electronic structure of InN,[4] the nitrogen antisite defect, N_{In}, was identified as producing deep levels in the 2 eV gap of InN and acting as a trap for both electrons and holes. On the other hand, the local density approximation (LDA) that is widely used in modern calculations of band structure predicts an occupied singlet state in the band gap, as well as an empty triplet state above the conduction band minimum (CBM).[5] The well-known problem of a severely underestimated band gap in LDA calculations was addressed in ref 5 by using the self-interaction and relaxation-corrected (SIRC) pseudopotentials. This approach gives a band gap energy of 1.3 eV for zinc blende InN while preserving the overall character of the defect-induced states from LDA.

The nitrogen vacancy, V_N, which behaves as a donor, has by far the lowest formation energy of all defects in InN.[4,5] This energy is, however, quite large (>2 eV), limiting the concentration of this native defect in as-grown samples to a very small level. All other native defects, characterized by prohibitively high formation energies, are expected to be present in as-grown samples only at negligible levels.[5] Consequently, most experimental studies of defects in InN would require an artificial creation of defects, similar to the case of GaN, where point defects have been intentionally created by high-energy electron irradiation.[6]

Point defects, such as interstitials and antisites, are also known to form quite efficiently in the nitride semiconductors under ion bombardment.[7] Both nitrogen interstitials, N_i, vacancies, V_N, and antisites, N_{In}, can be created simultaneously within the collision cascade by displacement of nitrogen atoms from their original lattice sites.

In the present letter, we report the direct observation of N_i and N_{In} as well as molecular nitrogen in ion-bombarded InN,

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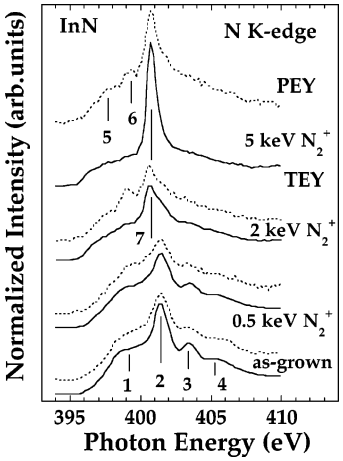

Figure 1. N K-edge NEXAFS spectra taken in TEY (solid line) or PEY (dotted line) modes from as-grown InN and surfaces bombarded with 2 or 5 keV N_2^+.

using synchrotron-based near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy. From NEXAFS spectra we have also determined the energy levels of defect-induced states within the band gap or the conduction band of InN. We compare our experimental results with SIRC calculations[5] and found a good qualitative agreement (in ref 5 only a relative energy scale is given for defect levels). To further support our assignment of new defect states in InN we have simulated NEXAFS spectra for small clusters of InN using a real-space multiple-scattering theory.[9] A good agreement with experimental results was obtained for clusters containing just N_i and N_{In}.

The InN(0001) samples used in this study were 750 nm thick and grown with unintentional n-type doping (carrier concentration of 10^{19} cm^{-3}) by plasma-assisted molecular beam epitaxy on a sapphire substrate with a GaN(0001) buffer layer.[8] All measurements were performed in a UHV chamber attached to beam line 24A1 of the National Synchrotron Radiation Research Center, Taiwan, equipped with a hemispherical electron analyzer for photoemission measurements, microchannel plates detector for NEXAFS measurements, and a low-energy ion gun for sample bombardment with nitrogen or argon ions. High-resolution NEXAFS measurements (energy resolution $\leq$60 meV) were carried out at VUV Photoemission beamline of Elettra, Italy.

NEXAFS spectra were recorded in both the surface-sensitive partial electron yield (PEY) (with a cutoff kinetic energy of 100 eV) and the bulk-sensitive total electron yield (TEY) around the nitrogen K-edge. The ab initio self-consistent FEFF8.2 code[9] based on multiple scattering theory was used for theoretical calculation of NEXAFS spectra in order to further support our assignment of the electronic structure of ion-bombarded InN.

In general, the nitrogen-related defects can be identified directly by NEXAFS measurements.[10,11] For transitions around the N K-edge, where the initial state is a 1s state, the final states must contain a contribution from p orbitals, for example in the form of $s+p_z$ (π^* transition) or p_x+p_y (σ^* transition).[11]

In Figure 1 we show some typical NEXAFS spectra, taken around the N K-edge at a photon impact angle of 40°, as measured from the sample surface, from both an as-grown InN surface and from surfaces bombarded for 15 min with N_2^+ ions at normal incidence. The raw NEXAFS data were fitted with a sigmoidal and several Gaussian line shapes (see Figure 2)[10,11] to determine the resonant energies, as listed in Table 1. The spectrum from the as-grown sample exhibits some characteristic σ^* (peaks 1,2 and 4) and π^* (peak 3) resonances,[12] originating

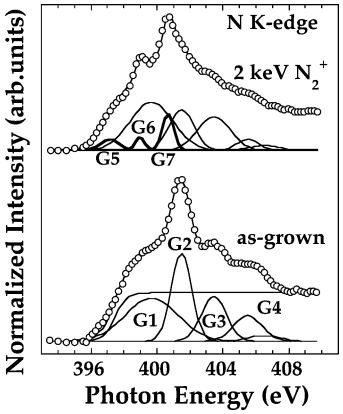

Figure 2. Fitting (solid lines) of the experimental PEY data (open circles) for the as-grown sample and sample bombarded with 2 keV N_2^+.

TABLE 1: Energy Position of Characteristic Features of the N K-Edge in InN

position	edge	1	2	3	4	5	6	7
energy (eV)	397.5	399.7	401.5	403.4	405.3	397.2	399.2	400.7

from transitions of N 1s core electrons to unoccupied p_{xy} or p_z states, respectively.[11,12] The absorption edge of 397.5 eV was determined from the inflection point of the sigmoidal that simulates transitions to the continuum.

After nitrogen bombardment, the NEXAFS spectra become broader, with resonant transitions 1−4 less pronounced. This observation is consistent with the expected increased amount of bombardment-induced disorder within the surface region.[10,13] In addition, three new peaks emerge in NEXAFS spectra from ion-bombarded surfaces: one at 0.3 eV below the absorption edge (peak 5 in Figure 1), and two above the absorption edge at 1.7 and 3.2 eV, respectively (peaks 6 and 7 of Figure 1, respectively). The peak at position 7 dominates NEXAFS spectra for 5 keV N_2^+ bombardment.

Before offering a possible explanation for the origin of new resonances in Figure 1, we note that the point defects that may have some empty states either in the band gap or the conduction band of InN include In and N antisites, vacancies, and interstitials.[4,5] As the final states of NEXAFS transitions around the N K-edge must include the contribution of N p-states,[11] In_N, V_{In}, In_i, and V_N defects cannot be observed around the N K-edge. This leaves N_i and N_{In} as the most favorable candidates for the point defects responsible for the new NEXAFS resonances in ion-bombarded InN.

To identify the transition responsible for resonance 6 of Figure 1, we first recall that the final empty state for this transition is placed high in the conduction band of InN, about 1.7 eV above the CBM. Such an energy position is in qualitative agreement with the SIRC calculation of N_{In} levels[5] that predicts a high-lying triplet state created by N_{In} in the conduction band (only a relative energy scale is given in ref 5). Therefore, we assign resonance 6 from Figure 1 to nitrogen antisites.

Turning now to resonance 5, we first note that the location of the final empty state of p-symmetry for this resonant transition is placed within the energy gap of InN, 0.3 eV below the CBM. As the existing theoretical models predict no defect states originating from antisites at this energy within the band gap,[4,5] we assign resonance 5 to N_i. A more detailed description of N_i defects in group-III nitrides is available in the literature only for GaN.[14] A split-interstitial configuration, in which two N atoms share the same substitutional site was identified as the interstitial state with the lowest formation energy, forming an

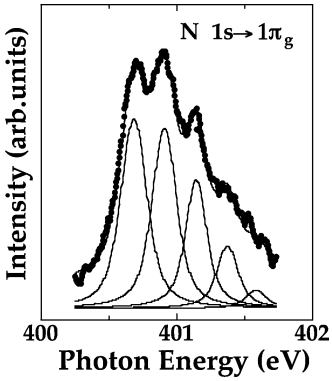

Figure 3. Vibrationally resolved N1s→$1\pi_g$ photoabsorption of molecular nitrogen (closed circles), measured at position 7 from an InN sample after 2 keV N_2^+ bombardment. Solid lines represent fitting using Voigt profiles with vibrational spacing of 225 meV.

empty state within the band gap of GaN.[14] We argue that the split interstitial may also form in InN and assign resonance 5 from Figure 1 to nitrogen split-interstitial.

Finally, we note that a sharp resonance at the same position as resonance 7 in Figure 1 has been observed previously in GaN[10,15] as well as InSb and InAs[16] and associated with the characteristic N1s→π^* transition in molecular nitrogen.[11] Therefore, we argue that the resonance 7 observed in our measurements is indeed a signature of molecular nitrogen in InN as the ion bombardment, in addition to producing N_{In} close to the surface (over the region overlapping with the damage profile), and can also break the nitrogen bonds to surrounding atoms and create molecular nitrogen.[16,17] Indeed, the high-resolution NEXAFS measurements of peak 7, shown in Figure 3, clearly show the characteristic vibrational structure of molecular nitrogen.[18]

To further support our assignment of new resonances in ion-bombarded InN, we have simulated the N K-edge absorption in InN using FEFF8.2.[9] We have first simulated the spectrum of an as-grown sample using several types of exchange-correlation potential, such as the Dirac−Fock, Hedin-Lundqvist, or Dirac-Hara potential,[9] for different clusters of up to 380 atoms, to determine the best fitting potential and the minimum cluster size that produce a good agreement with experiment.[19] In Figure 4a we compare the experimental PEY measurements from the as-grown InN with the theoretical simulation, using the Hedin−Lundqvist type of exchange-correlation potential for an InN cluster of 280 atoms.

The same type of potential and the cluster size has been applied to simulate the ion-bombarded surfaces, as shown in Figure 4b. Here, the theoretical curve II has been generated by addition of only two defects in the InN lattice: one nitrogen antisite, N_{In} (created by the replacement of one In atom with an N atom) responsible for resonance 5, and one split interstitial, N_{In} (in which each of two nitrogen atoms has two bonds to surrounding In atoms instead of four[14]) responsible for resonance 6. A very good agreement between experimental and theoretical NEXAFS structure just around the threshold energy fully supports our assignment of resonances 5 and 6 to N_{In} and N_i, respectively.

The above theoretical method cannot simulate the free N_2 at interstitial positions as it does not take into account the presence of a strong non muffin-tin effects in the local potential around N_2 defects.[9,19] Therefore, curve II in Figure 4b does not reflect the presence of N_2, characterized by the prominent resonance 7 in Figure 1. However, the contribution of N_2 to NEXAFS structure can be simulated by different methods, such as the finite-difference method (FDM),[20] that are not constrained to

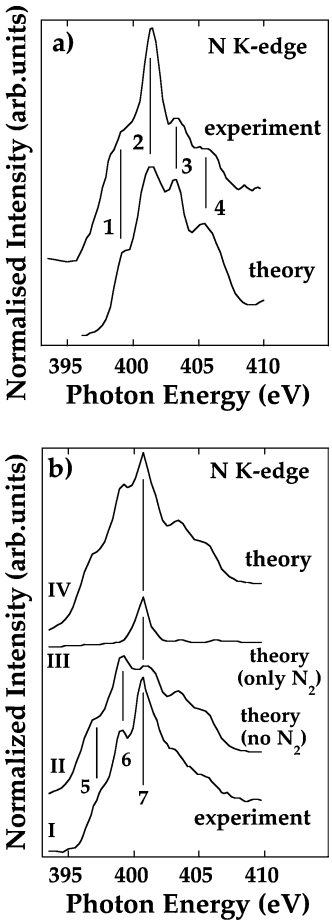

Figure 4. Comparison of experimental N K-edge NEXAFS spectra with theoretical simulations in (a) as-grown InN and (b) InN bombarded with 2 keV N_2^+ ions.

the muffin-tin approximation. Indeed, curve III in Figure 4b, representing the FDM simulation for free N_2 in InN,[19] is very similar to the low-resolution experimental data on gas-phase N_2 available in the literature.[18]

Curve IV in Figure 4b represents the superposition of FEFF and FDM simulations. It provides a very good agreement with the experimental spectrum I, thus supporting further our initial assignment of resonances in ion-bombarded InN to N_{In}, N_i, and N_2.

In conclusion, our NEXAFS measurements around the N K-edge of InN have provided the first direct experimental evidence and characterization of several defects created by ion-bombardment within the energy gap or the conduction band of InN. We assigned the states within the gap to nitrogen split-interstitials and supported our proposition with theoretical simulations using FEFF8.2.[9] The states within the conduction band are created by nitrogen antisites, in full agreement with recent theoretical calculations using SIRC pseudopotentials[5] and our theoretical simulations using FEFF8.2. We have also provided conclusive experimental evidence for the formation of molecular nitrogen in ion-bombarded InN, in full agreement with the theoretical simulation using FDM method.[19]

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