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Citation: Journal of Vacuum Science & Technology A **26**, 592 (2008); doi: 10.1116/1.2929851
View online: http://dx.doi.org/10.1116/1.2929851
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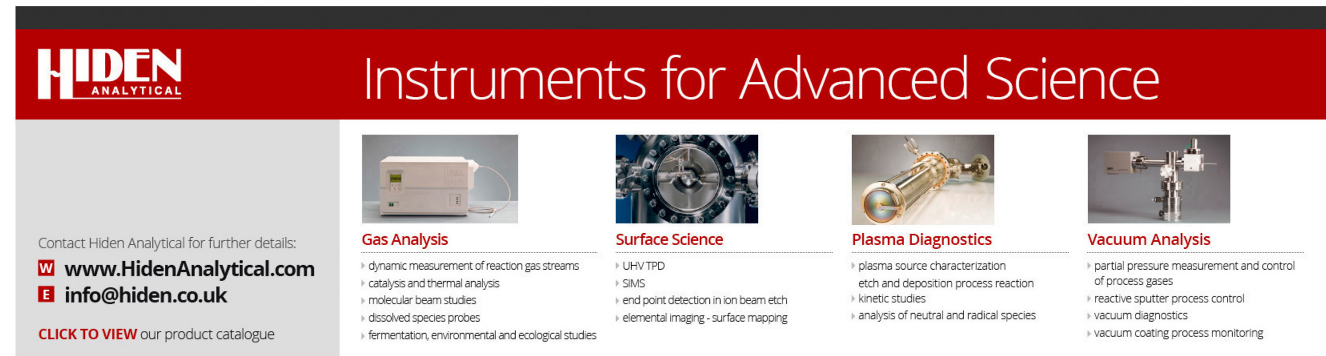

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Characterization of molecular nitrogen in III-V compound semiconductors by near-edge x-ray absorption fine structure and photoemission spectroscopies

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(Received 7 January 2008; accepted 21 April 2008; published 9 June 2008)

Formation of molecular nitrogen under low-energy nitrogen bombardment of III-V compound semiconductor surfaces has been studied by photoemission spectroscopy around N 1*s* core-level and near-edge x-ray absorption fine structure (NEXAFS) around N *K* edge. Interstitial molecular nitrogen N_2 has been formed in all of the samples under consideration. The presence of N_2 produces a sharp resonance in low-resolution NEXAFS spectra, showing the characteristic vibrational fine structure in high-resolution measurements, and at the same time, a new peak, shifted toward higher binding energies for several eV, in all N 1*s* photoemission spectra. © *2008 American Vacuum Society.* [DOI: 10.1116/1.2929851]

I. INTRODUCTION

The lack of lattice-matched substrates for the epitaxial growth of GaN and related nitrogen compounds has initiated the large effort in finding an appropriate method for nitridation of III-V semiconductors in order to produce thin nitride layers at the surface of host matrices.[1] Low-energy nitrogen implantation represents an attractive and feasible alternative to thermal or plasma-assisted nitridation and the application of ion beams in fabrication of surface nitrides has been explored on several compounds from the group III-V semiconductors.[2–4] For example, the formation of thin nitride layers has been observed by x-ray photoelectron spectroscopy (XPS) in nitrogen-bombarded surfaces of In-*V* compounds (V=As, P, or Sb).[3]

On the other hand, a new class of dilute III-V nitrides, such as GaN_xAs_{1-x}, has attracted considerable interest over the last few years, motivated primarily by the range of possible applications of these materials in optoelectronics and photonics.[5] At present, the bulk material of III-N-V alloys has not been reported, while expitaxial techniques such as molecular beam epitaxy or metal-organic chemical vapor deposition has been employed to grow thin films.[5] Again, low-energy nitrogen implantation represents an attractive alternative to epitaxial growth of diluted nitride layers. Indeed, diluted III-N-V alloys were synthesised by low-energy nitrogen implantation into GaAs, InP, InAs, and AlGaAs.[6,7]

Low-energy ion bombardment has also been widely employed during the growth and processing of thin films based on nitride semiconductors. For example, low-energy Ar^+ or N_2^+ ions are commonly used as a method of surface preparation (surface cleaning or ion-assisted etching) of GaN and related nitride compounds[8] that determines the final device structure.

However, the exposure of semiconductor surfaces to the low-energy nitrogen beam may introduce the formation of molecular nitrogen N_2 below the surface of the host lattice.[3] The presence of molecular nitrogen and related nitrogen bubbles can influence electrical, optical, or mechanical properties of the material.[9] Therefore, it is important not only to determine the chemical bonding of nitrogen to the host atoms, related to the formation of nitride films, but also to detect the possible presence of interstitial molecular nitrogen below the surface of samples bombarded by nitrogen ions.

In the present study, we have employed core-level photoemission spectroscopy and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, by using synchrotron radiation, to identify unambiguously the presence of molecular nitrogen introduced in several III-V semiconductors, such as GaSb, InSb, GaAs, InN, and GaN, by low-energy nitrogen bombardment.

II. EXPERIMENT

The samples used in this study were semi-insulating, undoped GaAs(100) and *n*-type InSb(111) and GaSb(100) wafers, while for comparison, we have also analyzed a nominally undoped, wurtzite GaN epilayer and a *n*-type InN(0001) film grown on sapphire substrates. All samples, transported in air to the synchrotron facility without receiv-

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ing any chemical or ion-beam cleaning prior to nitrogen bombardment, are referred to as "as-grown" samples.

All of the measurements were performed in an ultrahigh vacuum chamber attached either to the bending-magnet beam line 24A1 of the National Synchrotron Radiation Research Center, equipped with the hemispherical electron analyser for photoemission measurements and microchannel plates detector for NEXAFS measurements, or the undulator vuv Photoemission beam line of Elettra, equipped with an Omicron EA125 electron analyser for photoemission and NEXAFS measurements. The samples were bombarded with 2 to 5 keV N_2^+ or 2 keV Ar^+ ions at normal incidence using a low-energy ion gun.

Photoemission was taken around the N 1*s* core level with 550 or 600 eV photons. The photoemission spectra were normalized to the photoelectron current of the primary photon beam and then simulated with several sets of mixed Gaussian–Lorentzian functions.[10] The low-resolution NEXAFS spectra were recorded in the total electron yield mode around the nitrogen *K* edge, while the partial electron yield measurements were employed for the high-resolution NEXAFS.[11] The photon impact angle was 40°, measured from the sample surface.

III. RESULTS AND DISCUSSION

Synchrotron radiation-based spectroscopies are powerful tools for probing the electronic, physical, and chemical properties of metal or semiconductor surfaces.[12,13] In particular, NEXAFS spectroscopy is a useful technique for providing direct information about the electronic structure of materials and formation of molecular species in solid matrices.[13]

Bombardment of semiconductor surfaces with nitrogen ions can cause breaking of surface bonds and reaction of nitrogen with host atoms.[14–16] In addition, molecular nitrogen may form quite easily at interstitial positions due to the low formation energy of N–N bonds.[9] We have shown recently that the absorption of photons by nitrogen molecules formed in several compound semiconductors produces a characteristic resonance in NEXAFS spectra.[11] In this article, we complement NEXAFS with XPS measurements to examine possible chemical shifts in N 1*s* photoemission, related to N–N bonds in molecular nitrogen.[15]

We start with low-resolution NEXAFS of as-grown and ion-bombarded nitride semiconductors (GaN and InN) to define the characteristic resonance in nitrogen-bombarded samples, and then repeat the same measurements on some other III-V compounds (GaSb, GaAs, and InSb). In the second step, we undertake the high-resolution measurements to examine the possible vibrational structure of that characteristic resonance. Finally, we employ the photoemission measurements around N 1*s* core level to correlate the new features in photoemission with NEXAFS signature of molecular nitrogen.

In Fig. 1, we show some typical low-resolution NEXAFS spectra taken from both as-grown GaN and InN samples and from surfaces bombarded for 15 min with 2 keV N_2^+ ions. NEXAFS spectra of as-grown samples exhibit some characteristic σ and π resonances reflecting several possible transitions from the initial 1*s* state to the final states that contain contribution from *p* orbitals.[12]

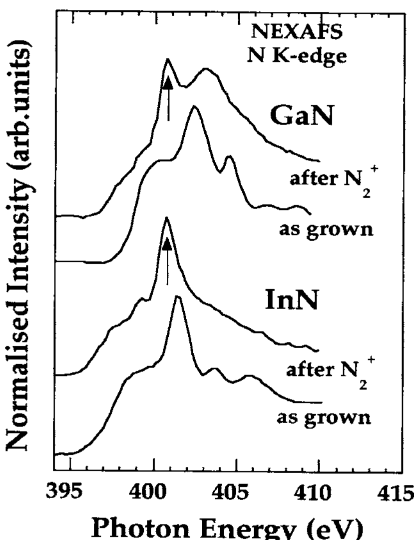

FIG. 1. N *K* edge NEXAFS spectra from as-grown InN and GaN and surfaces bombarded with 2 keV N_2^+ ions.

After 2 keV N_2^+ bombardment, NEXAFS spectra from Fig. 1 become broader, with resonant transitions less pronounced. This is consistent with the increased amount of disorder within the surface region.[17] In addition, both spectra in Fig. 1 exhibit a strong resonant peak around 400.8 eV. We note that a sharp resonance close to 401 eV have been observed previously in NEXAFS measurements from several different surfaces, such as CrN,[18] InSb,[11,15] ZnO,[11,16] or GaN,[11,19] irradiated with nitrogen ions. It has been associated with the characteristic N 1*s*-π^* transition in molecular nitrogen that is characterized by a sharp peak at around 400.8 eV.[12]

In addition, a high-resolution spectrum of this resonance peak, taken from a thin amorphous GaN films prepared by using an ion-assisted deposition (0.5 keV nitrogen beam),[20] or 3 keV N_2^+ ion bombardment,[11] exhibits the characteristic fine structure of vibrational levels in molecular nitrogen. Therefore, we argue that the sharp resonance observed in our measurements around 400.8 eV is indeed a signature of molecular nitrogen produced in GaN or InN by nitrogen bombardment. We expect to see its signature in XPS spectra as well.

In Fig. 2, we plot the photoemission spectra around N 1*s* core level from ion-bombarded samples from Fig. 1 on a relative binding energy (BE) scale with the zero point taken at the peak position of the dominant N–Ga or N–In component. Both emission curves (closed circles in Fig. 2) were deconvoluted into several sets of mixed Gaussian–Lorentzian functions originating from different nitride or oxynitride bonding.[21]

An additional peak shifted by 6.9 eV (for GaN) or 7.6 eV (for InN) toward higher BE is observed in both spectra. We assign this peak to molecular nitrogen in full agreement with NEXAFS spectra from Fig. 1.

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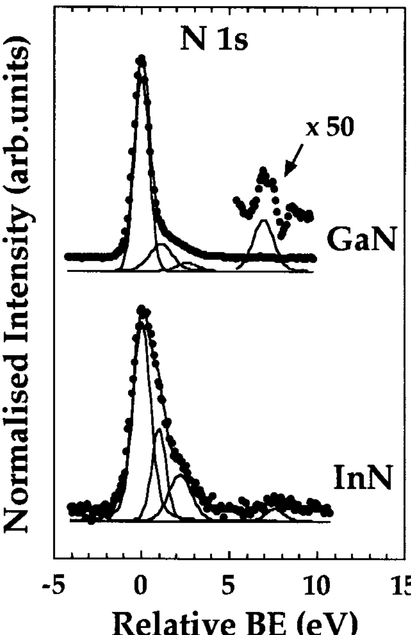

FIG. 2. N 1*s* core-level photoemission spectra (closed circles) obtained from GaN and InN surfaces bombarded with 2 keV N_2^+ ions. Solid lines are numerical fits of experimental curves.

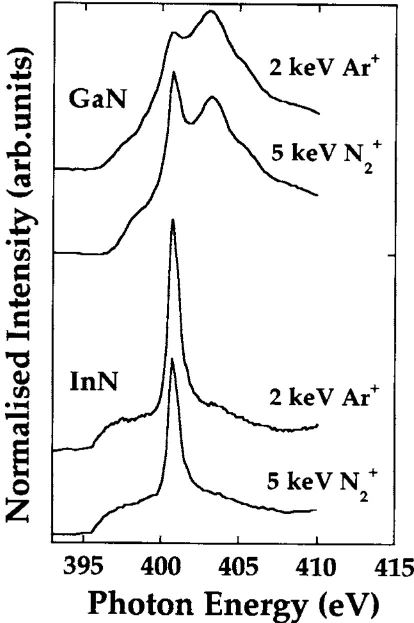

FIG. 3. Comparison of N *K* edge NEXAFS spectra from GaN and InN surfaces bombarded with 5 keV N_2^+ and 2 keV Ar^+ ions.

The contribution of nitrogen from the primary N_2^+ beam to the formation of molecular nitrogen depends on the efficiency of the ballistic mechanism within the host matrix (i.e., ion-induced mixing and relocation of host atoms), as the possible supply of nitrogen from the matrix may exceed the supply of nitrogen from the primary N_2^+ beam by several orders of magnitude. We illustrate this effect in Fig. 3 where we compare NEXAFS spectra of InN from surfaces bombarded with nitrogen and argon ions. A similar intensity of sharp resonance for Ar^+ and N_2^+ bombardment of similar ion energies (we note that 5 keV N_2^+ corresponds to 2.5 keV N^+) strongly supports the proposition about the dominant role of a ballistic mechanism in the formation of molecular nitrogen in InN under both Ar^+ and N_2^+ bombardment. In other words, most of the molecular nitrogen formed in InN under N_2^+ bombardment originates from the host nitrogen atoms as in the case of Ar^+ bombardment.

One would also expect the process of molecular nitrogen formation to be more efficient in compounds having a larger lattice constant and weaker metal-nitrogen bonds.[11] As GaN is thermodynamically more stable than InN and has a smaller lattice constant,[22] one expects a lower ratio of bond breaking to bond-formation process and less "free" space for molecular nitrogen in GaN, i.e., lower formation efficiency for molecular nitrogen in ion-bombarded GaN. This trend is evident in Fig. 3 in which we also display two NEXAFS spectra of GaN, bombarded simultaneously alongside the InN sample. Bombardment of GaN with Ar^+ ions produces a much smaller NEXAFS resonance than bombardment with N_2^+, indicating the weak role of a ballistic mechanism in the formation of molecular nitrogen in GaN. In other words, most of the nitrogen molecules formed in GaN under N_2^+ bombardment originates from the nitrogen ion beam.

The difference in formation mechanism of molecular nitrogen in GaN and InN is also evident in Figs. 1 and 2. We note that the strong N_2-related NEXAFS resonance in Fig. 1 dominates the spectrum from InN surface while it is less pronounced in GaN. At the same time, the intensity of N_2-related photoemission peak in Fig. 2 is much more pronounced in InN than in GaN (note the ×50 magnification in GaN spectrum).

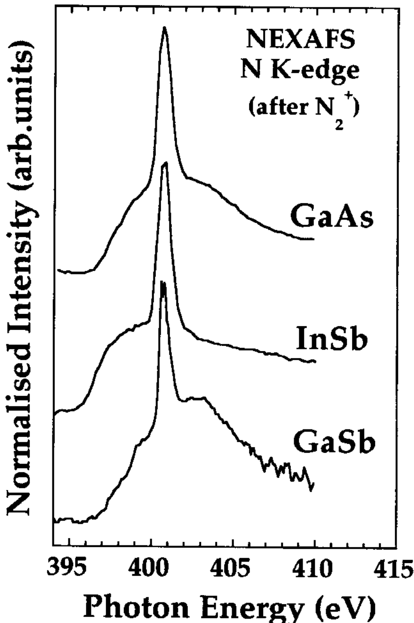

FIG. 4. N *K* edge NEXAFS spectra from GaSb, InSb, and GaAs surfaces bombarded with 3 keV N_2^+ ions.

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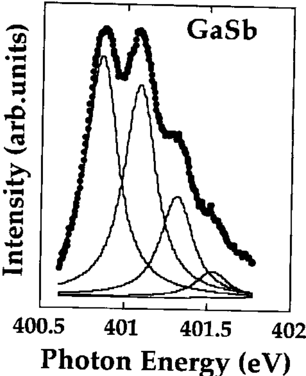

FIG. 5. Vibrationally resolved N 1*s*-π^* photoabsorption of molecular nitrogen (closed circles), measured at the sharp resonance in Fig. 4 from the GaSb sample after 3 keV N_2^+ bombardment. Solid lines represent fitting using Voigt profiles.

To further investigate the formation of molecular nitrogen in other III-V compounds, we have undertaken NEXAFS measurements around N *K* edge on GaAs, InSb, and GaSb bombarded with 3 keV N_2^+ ions. In Fig. 4, we summarize the low-resolution NEXAFS measurements. Again, all spectra are dominated by a strong resonance around 400.8 eV, we associate again with a characteristic N 1*s*-π^* transition in molecular nitrogen.

Indeed, high-resolution measurements over all resonances in Fig. 4 reveal the fine vibrational structure, as shown in Fig. 5 for GaSb. Here, we have used the Voigt profiles (solid lines in Fig. 5) to fit experimental data (closed circles in Fig. 5). The values obtained for the position of the first vibrational level (400.85 eV) and the separation of vibrational levels (233 meV) are very close to the vibrational structure of free N_2 molecules (400.868 eV and 235 meV, respectively[23]).

Again, we expect the signature of molecular nitrogen in photoemission spectra as well. In Fig. 6, we show the photoemission spectra around N 1*s* core level for samples from

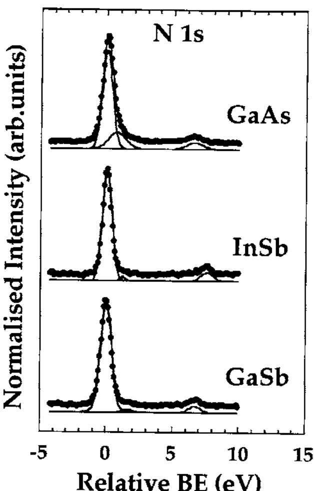

FIG. 6. N 1*s* core-level photoemission spectra (closed circles) obtained from samples from Fig. 4. Solid lines are numerical fits of experimental curves.

TABLE I. Chemical shifts of N_2-related peaks in photoemission spectra.

	GaN	GaSb	GaAs	InN	InSb
Shift from the dominant component (eV)	6.9	6.7	6.6	7.6	7.6

Fig. 4 on the same relative binding energy scale, as in Fig. 2. Indeed, we observe the additional peak, shifted toward higher binding energies by around 6.7 eV (for GaSb and GaAs) and 7.6 eV (for InSb). We note that chemical shifts of around 6.7 eV are the same for all Ga compounds, while shifts of around 7.6 eV are characteristic for all In compounds in Figs. 2 and 6, as listed in Table I.

IV. CONCLUSION

In summary, we have shown that NEXAFS and core-level XPS are complementary techniques that form a powerful combination for studying molecular nitrogen in III-V compounds. Molecular nitrogen forms at interstitial positions in all compounds and for all bombardment energies used in the present study, with a characteristic signature in both NEXAFS and XPS spectra. NEXAFS exhibits a sharp resonance at around 400.8 eV with the characteristic vibrational fine structure of N_2. XPS is characterized by the large chemical shift for N–N bonds of around 7.6 eV for In compounds and 6.7 eV for Ga compounds.

ACKNOWLEDGMENTS

The authors wish to thank G. Li of GuoKe Optronics and S. M. Durbin from the University of Canterbury for supplying the GaN and InN samples. This work was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program, and the Research Grant from the Ministry for Science, Education and Sport of the Republic of Croatia.

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