

Broadening of vibrational levels in X-ray absorption spectroscopy of molecular nitrogen in compound semiconductors

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Received 14 March 2006; in final form 12 May 2006

Available online 23 May 2006

Abstract

We have used high-resolution near-edge X-ray absorption fine structure spectroscopy to study the N 1s \rightarrow 1 π^* resonance of N₂ trapped below the surface of several compound semiconductors. The vibrational fine structure, observed from all samples under consideration, exhibits substantially larger lifetime linewidth Γ than in isolated N₂. A clear correlation between Γ and the lattice constant of the host matrix has been found, indicating that the broadening of vibrational levels is governed by a finite probability of the electron to escape from the π^* orbital into the matrix.

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The near edge structure of the X-ray absorption (XA) spectra of free molecules is characterised by the transition of core electrons into initially unoccupied, localised anti-bonding orbitals (π^* and σ^* resonances) or by excitations into Rydberg or multiple-electron states [1]. The corresponding spectra of physisorbed molecules, that are only weakly coupled to the substrate, are very similar to those from the gas phase [2–4].

Chemisorption is a different case. The XA spectra are generally simpler as the hybridisation of molecular orbitals with substrate levels suppresses most of the spectral features of isolated molecules, leaving only the π^* and σ^* resonances present in XA spectra [5].

Chemisorption of molecules, such as CO, N₂ or C₂H₄, has been studied in detail on several substrates by near-edge X-ray absorption fine structure (NEXAFS) [5–7]. The intensive π^* resonance, corresponding to the excitation of the 1s core electron into initially unoccupied molecular

orbitals of π symmetry, dominates the spectra around the K-edge. It has also been observed that the overall width of the π -resonance is much larger for chemisorbed molecules than for physisorbed or isolated molecules. This broadening has been explained either by the adsorbate–substrate hybridisation in the case of strong chemisorption or by vibrational excitations for weak chemisorption [6]. The reduced lifetime of the final excited state has also been considered as an alternative mechanism for the broadening of π -resonances [8].

No similar detailed studies are available in the literature for molecules buried into solid materials despite the fact that molecular species, such as N₂, have been observed in the bulk of several semiconductors, created either during the crystal growth or the oxidation process [9–11]. It is important to characterise the states of N₂ in solids not only because of the great technological significance of nitrogen-related defects as potential dopants or compensation centers in semiconductors, but also because of several interesting fundamental questions. Does the N₂ molecule, trapped within a solid, exhibit in general the same vibrational structure as the free N₂, or does it behave more as a chemi-

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sorbed or physisorbed molecule? How does N_2 interact with the surrounding matrix and does the matrix affect the N–N bond-strength or the lifetime of excited vibrational levels?

In this Letter, we address these questions by presenting synchrotron-based high-resolution NEXAFS measurements around the N K-edge of molecular nitrogen trapped below the surface of several compound semiconductors, including GaN, InN, ZnO, GaSb and InSb, most likely at interstitial positions [12]. Our measurements show that N_2 in all these compounds retain some of the properties of free molecules. However, we have observed for the first time significant broadening of individual vibrational levels that scales well with the lattice constant of the host matrix. This broadening is found to be consistent with the finite probability of an excited electron to escape from the π^* orbital into the matrix.

The samples used in this study were of hexagonal structure and include n-type films of GaN, InN and ZnO, grown on a-plane sapphire substrates, or n-type GaSb (100) and semi-insulating InSb (111) wafers. The lattice parameter, c , of these samples covers a wide range of values from around 5.2 Å in GaN to around 6.5 Å in InSb. The molecular nitrogen was created at room temperature within a thin surface layer of each sample by low energy nitrogen-ion bombardment (0.3–3 keV N_2^+) at normal incidence and for different bombardment times (5–30 min).

All measurements were carried out in a UHV chamber attached to the undulator VUV Photoemission beam line of Elettra, Italy, equipped with an Omicron EA125 electron analyser for photoemission and NEXAFS measurements and a low-energy ion gun for sample bombardment with nitrogen ions.

The high-resolution NEXAFS spectra, with photon energy resolution of about 60 meV for 20 $\mu\text{m}/20 \mu\text{m}$ opening of the beam-line slits, were recorded in the surface-sensitive partial electron yield (PEY) (with the kinetic energy of 50 eV) around the nitrogen K-edge. The photon energy scale was calibrated against the Fermi edge of a clean Au or Cu film in electrical contact with samples.

Vibrationally resolved NEXAFS spectra were fitted with Voigt profiles (a convolution of Lorentzians and Gaussians). The Gaussian width, related to the instrumental resolution, was kept constant at 60 meV, while the Lorentzian width, related to the natural line shape, was extracted from the line fits [1].

In Fig. 1, we show some typical low-resolution NEXAFS spectra taken from both an as-grown sample and from surfaces bombarded for 15 min with 2 keV N_2^+ ions. NEXAFS spectra of as-grown nitride semiconductors, like GaN or InN, exhibit some characteristic σ and π resonances reflecting several possible transitions from the initial 1s state to the final states that contain a contribution from p orbitals [1]. As an example, we show in Fig. 1 the NEXAFS spectrum taken from an as-grown GaN sample (curve a). Characteristic transitions to the final $s + p_z$ states, involving π -bonds (peaks 1 and 3) or $p_x + p_y$ states, involv-

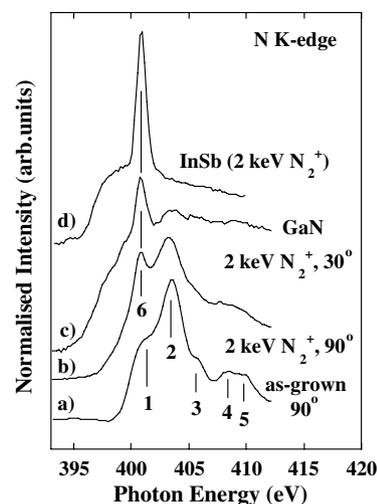


Fig. 1. N K-edge NEXAFS spectra taken from as-grown GaN and surfaces of GaN and InSb bombarded with 2 keV N_2^+ . The polarisation effect of NEXAFS spectra is illustrated for GaN with curves b and c.

ing σ -bonds (peaks 2, 4 and 5), known from the literature [1,13,14], are clearly resolved in this spectrum.

After nitrogen bombardment, the NEXAFS spectrum (curve b in Fig. 1) becomes broader with resonant transitions 1–5 spread out and less pronounced. This is characteristic of the increased amount of disorder within the surface region [15]. Indeed, XTEM measurements (not shown) have revealed an increased amount of damage in ion-bombarded samples. However, all samples preserved the overall crystallinity of surface region for ion-bombardment conditions used in our experiments.

In addition, a new intensive peak (peak 6 in Fig. 1) emerges in all ion-bombarded spectra at around 400.8 eV. Nitrogen bombardment of samples containing no nitrogen in their as-grown forms, such as ZnO, GaSb or InSb, produces the similar intensive peak in NEXAFS spectra, again around 400.8 eV, as shown in Fig. 1 (spectrum d) for an InSb sample. We note that this new resonance shows a strong π character, as illustrated by curves b and c in Fig. 1. At 90° (normal incidence of photons), the electron field vector of synchrotron radiation is parallel to the surface, favouring the excitation of in-plane σ -bonds, whereas at more oblique angles of incidence, such as 30° in Fig. 1 (curve c), there is a component of electric field perpendicular to the surface that will produce a more intensive signal from π -bonds [1]. Indeed, the resonance 6 is more intensive for 30° than 90°, clearly indicating the π character of bonds involved in this transition.

The strong resonance 6, found in our experiments in all samples bombarded with nitrogen ions (even for 0.3 keV N_2^+ bombardment for 5 min), has been associated previously with the characteristic $N1s \rightarrow \pi^*$ transition in molecular nitrogen [10,12,14,16]. First principle calculations based on density functional theory have also shown that the dominant N-related defect (i.e. the defect with the lowest formation energy) in heavily N-doped compound semiconductors is in fact the N_2 defect [17].

Indeed, a high-resolution scan over the resonance 6 reveals the fine structure characteristic for the excitation of nitrogen 1s core electrons into unoccupied orbitals of π symmetry of molecular nitrogen [18], as shown by closed circles in Fig. 2 for InSb bombarded with 3 keV N_2^+ ions. An analysis of high-resolution data using Voigt profiles (full lines in Fig. 2) has given the position of the first vibrational level at 400.85 eV and the separation of vibrational levels, ω_e , of 233 meV. These values are very close to the vibrational structure of isolated N_2 molecules (400.868 meV and 235 meV, respectively [18]). Further, the strong π character of resonance 6 (see Fig. 1) corresponds to N–N bonds oriented along the c -axis, i.e. along the direction that provides the most space for N–N bonds in a hexagonal matrix.

On the other hand, the full width at half maximum, Γ , of inherent Lorentzian linewidth of 190 meV, extracted from the fit in Fig. 2, is substantially larger than the characteristic value of Γ found for gaseous N_2 molecules (132 ± 8 meV [18–20]). The increased value of Γ indicates that some additional decay channels are available to N_2 within the InSb matrix compared with isolated N_2 molecule. To further investigate these new channels, we compare in Fig. 3 the vibrationally resolved N 1s $\rightarrow 1\pi^*$ photoabsorption of N_2 trapped below the surface of several semiconductors of different lattice constant, c . In Fig. 3, we also show for comparison the high-resolution NEXAFS spectrum taken on the same beamline from the gaseous molecular nitrogen [20].

The values of Γ and ω_e , extracted from the NEXAFS profiles in Fig. 3, are listed in Table 1 together with lattice parameters, c , of host matrices. We point out here that quite similar parameters have been extracted from spectra taken from several samples in the bulk-sensitive total electron yield (TEY) mode, indicating that the proximity of surface in our PEY measurements does not influence significantly the results shown in Figs. 1 and 3. This observation is consistent with our previous measurements on InN [21].

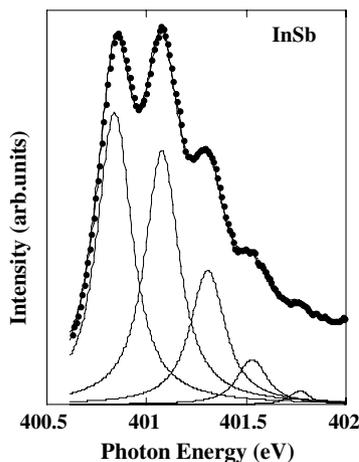


Fig. 2. Vibrationally resolved N1s $\rightarrow 1\pi_g^*$ photoabsorption of molecular nitrogen (closed circles), measured at position 6 from an InSb sample after 3 keV N_2^+ bombardment. Solid lines represent fitting using Voigt profiles.

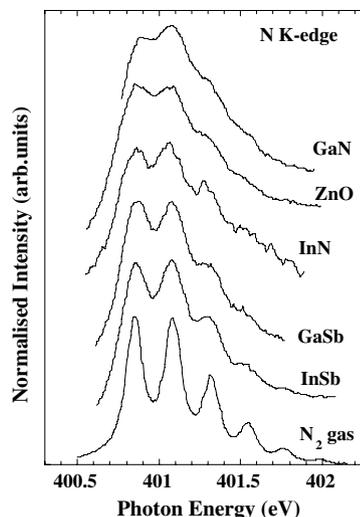


Fig. 3. Vibrationally resolved NEXAFS data from N_2 trapped in different compound semiconductors bombarded with 3 keV N_2^+ ions for 15 min. A spectrum from gaseous N_2 is shown for comparison.

The energy position and the separation, ω_e , of vibrational levels of N_2 in all compounds examined in this work remain constant (within the experimental error) and almost identical to the case of isolated N_2 . This observation strongly supports the assertion that the molecular nitrogen forms in all compounds shown in Fig. 3 after nitrogen-ion bombardment. As the separation of vibrational levels reflects the strength of intramolecular bonds [7], this later observation provides evidence that the surrounding matrix does not change the strength of N–N bonds in molecules trapped within compound semiconductors examined in the present work. This is also consistent with the orientation of N–N bonds along the longest, c -axis of the hexagonal crystal that would minimise any stress on the molecule.

In contrast, an earlier study of oxidised TiAlN films [9] has shown a significant increase in vibrational separation compared to free N_2 , consistent with the stress on the interstitial N_2 by the surrounding matrix that may strengthen the N–N bonds.

Returning back to Table 1, we further notice that the linewidth Γ increases as the lattice constant, c , of the host matrix decreases. In other words, broadening of vibrational levels is more pronounced in compounds that offer less space for molecular nitrogen along the c -axis.

In order to explain the broadening mechanism of vibrational levels, we first note that the overall width of all π -resonances (see Figs. 1 and 3) remains constant (FWHM of about 0.65 eV was determined from both low- and high-

Table 1
Lifetime width (Γ) and vibrational constant (ω_e) for the N 1s $\rightarrow 1\pi_g^*$ transitions of N_2 trapped in different hexagonal matrices of lattice constant c

	GaN	ZnO	InN	GaSb	InSb	N_2 gas [17]
Γ (meV)	280	260	225	210	190	132 ± 8
ω_e (meV)	236	236	232	230	233	235
c (Å)	5.18	5.21	5.7	6.1	6.48	∞

resolution measurements). This observation is consistent with the weak interaction between the molecular orbitals of N_2 and the orbitals of the host atoms. In contrast, chemisorption of CO molecules on Ni (100) surface gives rise to the formation of new π -d hybrid states through a strong interaction between molecular $2\pi^*$ orbitals of CO and partially filled Ni 3d orbitals, forming a continuum of adsorbate-substrate (CO-Ni) states and causing a substantial overall broadening of the corresponding π -resonance of CO [6].

The situation is quite different for chemisorption on substrates of essentially filled d bands, such as Ag or Cu. In this case the hybridisation with the substrate is very small as the s and p hybrids form considerably weaker bonds with molecular orbitals, leading to less broadening of corresponding π -resonances [6]. However, even in the case of a weak interaction, the overall width of a π -resonance of a chemisorbed molecule is still larger than the corresponding width of a free-molecule resonance [6].

In our case, the d bands (3d or 4d) of all metals (Ga, In, Zn, Sb) involved in the compound matrices are filled and, if any hybridisation takes place, one expects only a weak interaction involving s and p orbitals of host atoms. However, all π -resonances in our study exhibit almost the same full width at half maximum (of about 0.65 eV) as the gaseous N_2 (see Fig. 3), indicating little, if any, hybridisation between molecular and metallic orbitals.

We note that a weak interaction between molecular nitrogen, trapped in a disordered GaN:O film, and the host matrix was proposed in a recent study of the structure of GaN:O films prepared in the presence of energetic beam of nitrogen ions that introduces molecular nitrogen into the matrix [10].

The correlation between the lattice constant c and the vibrational broadening of N_2 levels (see Table 1) may be described in terms of a hopping process for the excited electrons from π^* orbitals. We characterise the transfer rate, or the probability of an excited electron to escape from the π^* orbital into the matrix, by a simple exponential law, $\exp(-d)$, where d is the barrier width for the transition, proportional in our case to the distance between a N_2 molecule and the surrounding atoms along the c -axis, i.e. to the lattice constant c . In this picture, the linewidth broadening will depend on the final-state lifetime [8]. The escape of a π^* -electron, favoured for the closer distance between N_2 and matrix atoms, reduces the lifetime of final states and increases the linewidth Γ . Indeed, the linewidth Γ from Table 1 exhibits a linear dependence on $\exp(-c)$, as shown in Fig. 4.

Interpolation of this linear relationship to zero (i.e. to the case of an infinite lattice constant, $c = \infty$) corresponds to the Γ value of gaseous N_2 from the literature [18], as shown with an open circle in Fig. 4. Indeed, a free N_2 molecule provides no additional channels for escape of excited electrons, which can be described by the infinite barrier width, or infinite lattice constant, $c = \infty$, for transitions into the ‘matrix’.

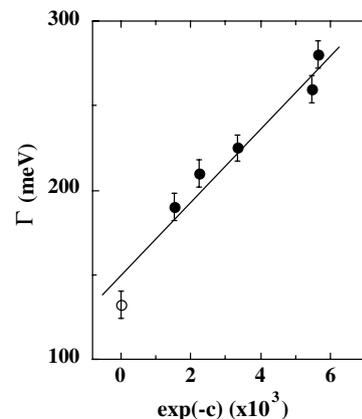


Fig. 4. Natural linewidth, Γ , as a function of $\exp(-c)$, where c is the lattice constant of hexagonal matrices from Table 1. Solid line serves as a guide for eye.

We conclude that molecular nitrogen forms quite efficiently at interstitial positions below the surface of compound semiconductors under low-energy nitrogen bombardment due to the low formation energy for N_2 . The molecules are preferentially oriented along the c -axis of hexagonal samples as this direction provides the most space for N-N bonds. No significant interaction of molecular nitrogen with the surrounding lattice or formation of new hybrid states was observed for N_2 trapped in compound semiconductors. However, vibrationally resolved photoabsorption data have revealed significant broadening of individual vibrational levels which scales well with the lattice constant c of the host hexagonal matrix. This observation is found to be consistent with the finite probability, governed by a simple exponential law, $\exp(-c)$, of an electron to escape from the π^* orbital into the matrix.

Acknowledgements

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.

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