Characterisation of nitrogen-related defects in compound semiconductors by near-edge x-ray absorption fine structure

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Abstract—We have studied the formation of nitrogen-related defects created in compound semiconductors by low-energy ion bombardment (0.3-5 keV N$_2^+$ or Ar$^+$) using near-edge x-ray absorption fine structure (NEXAFS) around the N K-edge. Nitrogen interstitials and antisites have been identified in NEXAFS spectra of InN and GaN in full agreement with theoretical calculations. Several defect levels within the band gap and the conduction band of GaN and InN were clearly resolved in NEXAFS spectra. We attribute these levels to interstitial and antisite nitrogen in good agreement with theoretical calculations. Interstitial molecular nitrogen, N$_2$, has been observed in all 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.

Keywords—InN, GaN, InSb, GaSb, GaAs, ZnO; NEXAFS; nitrogen interstitials; nitrogen antisites; molecular nitrogen; low-energy ion bombardment

I. INTRODUCTION

To fully realise the potential of GaN and InN, as well as their ternary alloy InGaN, a fundamental understanding of point defects is required, as these may control some vital characteristics of nitride semiconductors, ranging from the type of conductivity to dopant diffusion. The large formation energies of point defects in nitride semiconductors prevent efficient formation of native defects in as-grown samples, limiting their concentrations to very small or negligible levels [1,2]. Consequently, most experimental studies of point defects would require an artificial creation of defects, for example by high-energy electron or low-energy ion irradiation [3,4].

In the present paper, we report the direct observation of nitrogen interstitials and antisites as well as molecular nitrogen in ion-bombarded GaN and InN, using synchrotron-based near-edge x-ray absorption fine-structure (NEXAFS) spectroscopy. From NEXAFS spectra we have determined the energy levels of defect-induced states within the band gap and the conduction band of GaN and InN, in a good agreement with theoretical calculations. We also show that the exposure of GaN and InN, as well as some other non-nitride semiconductors, such as GaAs, InSb, GaSb or ZnO, to the low-energy nitrogen beam may create molecular nitrogen, N$_2$, below the surface of the host lattice.

II. EXPERIMENT

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 GaAs (100) and InSb (111) wafers.

The low-resolution NEXAFS 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 analyser for photoemission measurements, microchannel plates detector and a low-energy ion gun for sample bombardment with nitrogen or argon ions. 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 high-resolution NEXAFS spectra were taken in a UHV chamber attached to the undulator VUV Photoemission beam line of Elettra, Italy, equipped with an Omicron EA125 electron analyser. The raw NEXAFS data were normalized and fitted with a sigmoidal and several Gaussian lineshapes to determine the absorption edge and the resonant energies of different peaks in NEXAFS spectra.

III. RESULTS AND DISCUSSION

In general, the nitrogen-related defects can be identified directly by NEXAFS measurements [5,6,7]. 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 $s^+p_z$ ($\pi^*$ transition) or $p_z^+p_y$ ($\sigma^*$ transition) [5].

In Fig.1 we show some typical low-resolution NEXAFS spectra taken from an as-grown GaN sample and from the surface bombarded for 15 minutes with 2 keV N$_2^+$ ions. NEXAFS spectrum of as-grown sample exhibits some characteristic $\sigma$ and $\pi$ resonances (Gaussians 1-5 in Fig.1)
reflecting several possible transitions from the initial 1s state to the final empty states that contain a contribution from p orbitals [5].

After nitrogen bombardment, the NEXAFS spectrum 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 [7,8].

The good fit of the ion-bombarded spectrum in Fig.1 was possible by keeping at fixed energies the position of original Gaussians, G1-G5, and sigmoidal (thin solid lines) and introducing three additional Gaussian functions, P1-P3 (thick solid lines in Fig.1). The energy positions of these additional features are listed in Table I.

In Fig.2 we show the NEXAFS spectra taken from both an as-grown and ion-bombarded InN sample. As in the case of GaN, the NEXAFS spectra from InN were fitted with a sigmoidal and several Gaussian functions, with additional three Gaussians, P1-P3, required for a good fit of the ion-bombarded spectrum.

In the case of GaN from Fig.1, the location of the final empty states of p-symmetry for resonant transitions P1 and P2 is clearly placed within the energy gap of GaN at 1.5 eV and 0.2 eV below the conduction band minimum (CBM), respectively. The existing theoretical models, using, for example, ab initio molecular dynamics calculations [9] or first-principle total-energy calculations [10], predict several empty defect states within the energy gap of GaN accessible for NEXAFS transitions around the N K-edge. For example, a defect state originating from nitrogen antisites, N\(_{Ga}\), forms an empty doublet at 0.2 eV below the CBM. On the other hand, a split-interstitial configuration in which two N atoms share the same substitutional site was identified theoretically as the interstitial state, N\(_i\), with the lowest formation energy, forming an empty state within the bandgap of GaN at 1.3-1.8 eV below the CBM.

### Table I.

<table>
<thead>
<tr>
<th>Edge (eV)</th>
<th>InN</th>
<th>GaN</th>
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<tbody>
<tr>
<td>P1 (eV)</td>
<td>397.7</td>
<td>399.0</td>
</tr>
<tr>
<td>P2 (eV)</td>
<td>399.0</td>
<td>399.0</td>
</tr>
<tr>
<td>P3 (eV)</td>
<td>400.8</td>
<td>400.8</td>
</tr>
</tbody>
</table>

Energy positions of characteristic features of the N K-edge in InN and GaN.
As the resonance P2 of GaN emerges at exactly 0.2 eV below the CBM, we assign this resonance to an antisite nitrogen defect, N_{Ga}. At the same time, the energy position of resonance P1 coincides with the energy range predicted theoretically for N_{i} [9,10], so we assign P1 to the split-interstitial configuration of nitrogen.

Turning now to the ion-bombarded InN in Fig.2, we note that the location of resonances P1 and P2 is placed at 0.3 eV below the CBM and 1.7 eV above the CBM, respectively. The energy position of P2 is in qualitative agreement with the theoretical calculation of nitrogen antisite, N_{In}, levels [2] that predicts a high-lying triplet state created by N_{In} in the conduction band (only a relative energy scale is given in [2]). Therefore, we assign the resonance P2 in InN to nitrogen antisites.

On the other hand, the existing theoretical models predict no defect states originating from antisites within the energy gap of InN. Therefore, in analogy to GaN, we assign the resonance P1 in InN to N_{i}.

Finally, we note that a sharp resonance at the same position as resonance P3 in Figs.1 and 2 has been observed in a range of compound semiconductors bombarded by the low-energy nitrogen ions, as shown in Fig.3 for GaSb, InSb, GaAs and ZnO. This resonance has been associated with the characteristic N1s→π* transition in molecular nitrogen [11,12]. Therefore, we argue that the resonance P3 observed in our measurements is indeed a signature of molecular nitrogen created during ion bombardment. Indeed, the high-resolution NEXAFS measurements of peak P3, shown in Fig.4, clearly show the characteristic vibrational structure of molecular nitrogen [11].

In conclusion, our NEXAFS measurements around the N K-edge have provided the direct experimental evidence of several defects created by ion-bombardment within the energy gap or the conduction band of GaN and InN. We assigned these states to nitrogen split-interstitials or antisite nitrogen, in full agreement with some theoretical calculations. We have also provided conclusive experimental evidence for the formation of molecular nitrogen in a range of ion-bombarded compound semiconductors.

IV. CONCLUSION

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REFERENCES