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Short communication

Near-edge X-ray absorption fine-structure studies of GaN under low-energy nitrogen ion bombardment

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Abstract

The electronic structure of p-type GaN layers exposed to low-energy nitrogen ion bombardment was studied by near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy. It was found that ion bombardment lead to the creation of states lying below the nitrogen absorption edge which posses p-symmetry. These states are attributed to nitrogen interstitials with different local topologies created during ion bombardment. Furthermore, the NEXAFS spectra also shows the development of a strong π^*-resonance above the absorption edge with increasing incident nitrogen ion energy. This peak is attributed to the formation of molecular nitrogen at interstitial positions, arising from a build up of nitrogen ions on these sites.

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1. Introduction

GaN and other nitride based semiconductors are currently the most promising materials for a range of wide band-gap devices, including blue and ultraviolet light-emitting diodes, laser devices and even high-efficiency solar cells [1]. Recent advances in growth technology of these compounds has produced high quality layers, enabling such devices to be realized [2]. As with all semiconductor devices, both surface treatments during processing and ion implantation are key processing steps in device fabrication. These procedures may result in the creation of many defects in GaN, and it is thus imperative to determine the

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properties and to understand the impact of defects upon the electronic structure of GaN to ensure that device integrity is not compromised.

It has been shown recently that a low-energy Ar^+ bombardment of GaN can lead to the creation of some interstitial nitrogen and also molecular nitrogen below the surface [3,4]. In the present study we extend this previous work to the nitrogen bombardment of GaN that may increase the nitrogen content in the near-surface region and possibly create more nitrogen interstitials or molecular nitrogen. In the present paper we report on the observation of nitrogen interstitials, N_I, and molecular nitrogen in p-GaN under low-energy N_2^+ bombardment. We have employed synchrotron-based near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy around the nitrogen K-edge to determine changes in the electronic structure of bombarded surfaces and to identify the defects responsible for these changes.

Synchrotron radiation-based spectroscopies are powerful tools for probing the electronic, physical and chemical properties of semiconductor surfaces [5]. In particular, NEXAFS spectroscopy is a useful technique for providing direct information about the electronic structure of materials. By probing very close to the absorption edge of different atoms, it is possible to construct an electronic model of the valence and near band-edge states associated with the target atom species. Furthermore, the polarized nature of synchrotron radiation means that the relative symmetry and local bonding environment of these states can also be probed by examining the effect of changing the angle of radiation incidence on the spectral features. π^*- and σ^*-resonances have very different NEXAFS signatures [5], enabling the changes in crystallographic directions or in the local environment induced by ion bombardment to be detected.

2. Experimental

The samples used in this study were 2 μm thick p-type (Mg-doped, 5×10^{19} Mg cm^{-3}) GaN epi-layers grown on *c*-axis sapphire by metallorganic chemical vapour deposition. All measurements were performed in the UHV main chamber of the 2B1 beam line at the Pohang Light Source. A low energy (0–2 keV) ion-gun was used for N_2^+ bombardment at normal incidence. NEXAFS spectra were recorded in the total electron yield (TEY) mode around the nitrogen K-edge. The angle of photon beam incidence was varied to determine the symmetry of introduced states. In this case, all measured angles are given as the angle of the beam from the sample surface. Prior to analysis, all raw NEXAFS data was normalized in the way described previously [3]. Gaussian lineshapes were used to fit the curves, as these best simulate the resonant transition to bound final states observed in the spectra [3,6].

3. Results and discussion

NEXAFS spectra of as-grown p-GaN, and p-GaN bombarded with 0.3, 1 and 2 keV N_2^+ for 30 min for a photon incidence of 35° to the sample surface is shown in Fig. 1. Also shown is the NEXAFS spectra for the same sample bombarded with 2 keV Ar^+ under the same conditions.

The spectrum from the as-grown samples exhibits characteristic π^* (peaks 1 and 3 in Fig. 1) and σ^*(peak 2) resonances (see also Fig. 2) [3,4,6]. From the as-grown data, we find the absorption edge to be

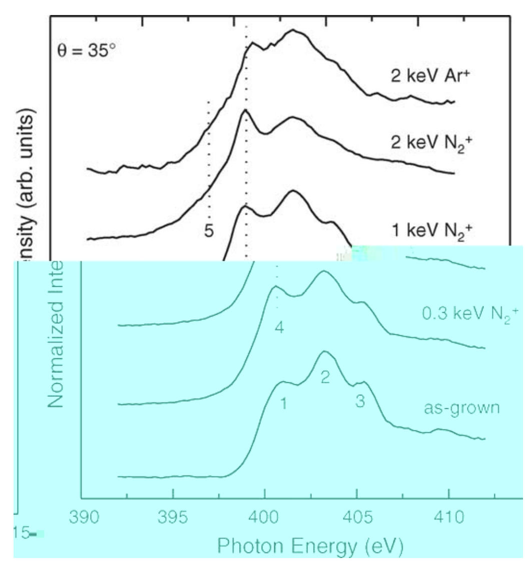

Fig. 1. Normalized N K-edge NEXAFS spectra from as-grown and ion bombarded p-GaN. All samples were bombarded for 30 min, and spectra were taken for the photon incidence angle of 35° with respect to the sample surface.

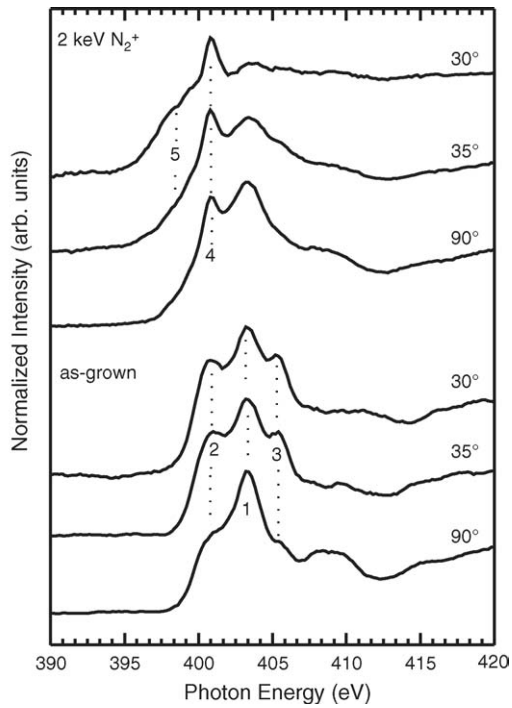

Fig. 2. Polarization dependence of N K-edge NEXAFS spectra of as-grown and 2 keV N_2^+ ion bombarded samples. At the low (grazing) angles of 35° and 30°, features 4 and 5 become more prominent, indicating their π^*-symmetry.

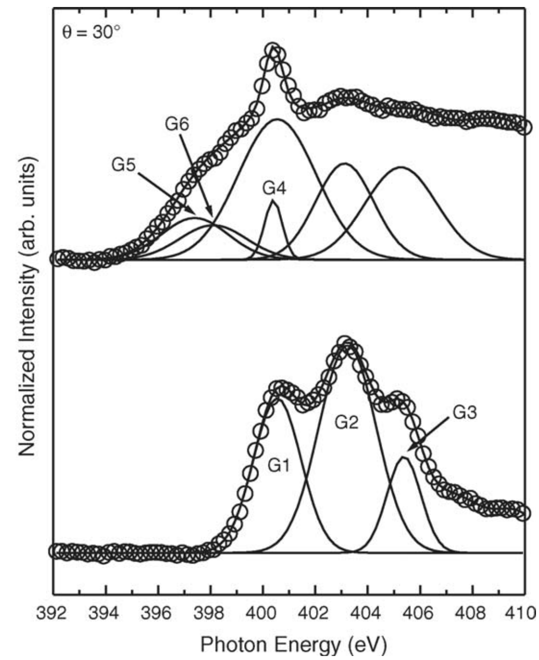

Fig. 3. Normalized N K-edge NEXAFS spectra from as-grown and 2 keV nitrogen ion bombarded p-GaN taken a photon impact of 30°. The solid lines are a numerical fit of the experimental data (open circles). The introduction of three new resonances G4, G5 and G6 are evident with ion bombardment.

399.5 eV as determined from the inflection point of the leading edge of the NEXAFS spectrum. With increasing energy of nitrogen ion bombardment, three features of the spectra become evident. Firstly, it is noted that the characteristic resonant peaks in the NEXAFS spectra appear to be much broader. This can be attributed to increased disorder at the surface as a result of ion bombardment which results in a broadening of the resonant transitions [4].

Secondly, the formation of a shoulder-type feature emerges around 398.5 eV (below the absorption edge), and thirdly, a strong resonance at 400.4 eV (above the absorption edge but 0.2 eV below the original resonance 1) is seen to become more prominent with increased bombardment. This increased prominence is not seen for the sample bombarded with argon ions (see Fig. 1).

Fig. 2 shows a comparison between spectra taken at different angles (30°, 35° and 90° to the sample surface) for both as-grown and 2 keV N_2^+ bombarded samples. From this graph we see that features 2–5 all become more prominent for spectra taken for grazing incidence angles, thus possessing π^*-bonding symmetry. Meanwhile, feature 1 remains more pronounced at normal incidence and can thus be attributed as a σ^*-resonance.

Finally, in Fig. 3 we show a numerical fit for the NEXAFS spectra taken at 30° from both the as-grown sample and the sample bombarded with 2 keV N_2^+ for 30 min. The spectra have been fitted with Gaussians to simulate the resonant transitions from the initial N 1s core state to the final states of p-symmetry in the conduction band or within the energy gap [6]. Only the three dominant transitions are shown for the as-grown sample (G1–G3). To fit the ion-bombarded sample, the peak positions of G1–G3 were kept fixed. In order to obtain a good fit of the experimental data, three new Gaussian functions were required. Firstly, G4, a sharp resonance 0.2 eV below peak G1 and $\sim$1 eV above the absorption edge, and secondly two broader resonances, G5 and G6 that fall below the absorption edge. G5 is located at 397.4 eV which is 2.1 eV below the absorption edge and G6 is at 398.1 eV which is 1.4 eV below the absorption edge. The location of G5 and G6 below the absorption edge indicates that the final empty states of p-symmetry for these transitions are within the band-gap of GaN. For a band-gap of 3.4 eV, we get an energy position for these states of 1.3 and 2.0 eV above the valence band maximum (VBM) respectively. These values are in good agreement with theoretical calculations for N_I states in GaN [7,8] and we associate peaks G5 and G6 to nitrogen interstitials with different local topologies.

On the other hand, it is reasonable to assume that the build-up of interstitial nitrogen, originating from both the nitrogen beam and the relocated matrix atoms, would eventually produce molecular nitrogen, N_2, trapped at interstitial positions. Therefore, we associate the sharp resonance G4 with the molecular nitrogen formed in GaN under N_2^+ bombardment.

We note that this assignment is in agreement with some previous NEXAFS studies. For example, a spectrum from a thin amorphous GaN films prepared using an ion-assisted deposition (0.5 keV nitrogen beam) [9] exhibits a peak at position similar to G4 that has been associated with the presence of nitrogen bubbles in amorphous GaN film, but no explanation was given for the origin of this effect. A very intensive resonant peak at position similar to G4, that has been tentatively associated with the molecular nitrogen, has also been observed in InSb and InAs bombarded by 500 eV N_2^+ [10].

4. Conclusions

In conclusion, we have employed NEXAFS spectroscopy to characterize p-type GaN exposed to nitrogen ion bombardment. We have shown that bombardment results in the formation of interstitial levels within the band-gap which have π^*-symmetry. These levels are located at 1.3 and 2.0 eV above the VBM, respectively (for a 3.4 eV band-gap). We have also shown that molecular nitrogen, also found to posses π^*-symmetry, may form within GaN under nitrogen ion bombardment.

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