N - K edge NEXAFS study of the defects induced by indium implantation in GaN

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Abstract. N - K edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy is applied in order to determine implantation-induced changes in the electronic structure of GaN. The samples were implanted with 700 keV In ions and fluencies in the range 5×10^{13} – 1×10^{16} ions/cm^2. The NEXAFS results are discussed in combination with Rutherford backscattering (RBS) characterization which assesses the implantation induced damage. The main implantation effects on the NEXAFS spectra are: (a) a fluence-dependent broadening of the NEXAFS peaks, (b) emergence of a pre-edge shoulder (RL1) that is attributed to N split-interstitials and (c) appearance of a post-edge sharp peak (RL2) that is attributed to molecular N_2 trapped in the GaN matrix. The RL2 is characterized by fine structure due to vibronic transitions that result from a change of the vibrational quantum number along with the electronic transition. The concentration of the interstitials and the N_2 molecules as well as the width of the NEXAFS peaks, have a sigmoidal dependence on the logarithm of the ion fluence, following the behaviour of the defect concentration deduced from the RBS measurements.

1. Introduction

The ternary semiconductor $In_xGa_{1-x}N$ has a direct bandgap that varies with x and spans the whole visible spectrum. Therefore, InGaN/GaN heterostructures find applications in the fabrication of opto- and microelectronic devices [1] while enhancement of the emission characteristics has been observed in InGaN quantum dots [2]. Ion implantation is an attractive method for the synthesis of semiconductor heterostructures, as for example Si_xGe_y/Si [3-5], since it allows precise control of the implant dose and profile. Thus, implantation of GaN with In is a potential method for the fabrication of InGaN/GaN nanostructures. The main disadvantage of ion implantation is the induced lattice damage [6] which can be partially recovered after annealing at high temperatures. Here we apply near edge X - ray absorption fine structure spectroscopy (NEXAFS) at the N - K edge in order to study the effect of In implantation, with fluences that vary over 3 orders of magnitude, on the electronic structure of GaN. The NEXAFS results are discussed in combination with the defect concentration

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which was estimated from Rutherford backscattering (RBS). The NEXAFS spectra recorded at the K edge of low-Z elements are characterized by fine structure due to the large core-hole lifetime of the 1s electrons. It has been demonstrated that the N-K edge NEXAFS spectra of group III nitrides are sensitive to the symmetry, the composition and the formation of detects [7-9].

2. Growth conditions and experimental details

The 450 nm - thick GaN layer was grown on (0001) Al_2O_3 by plasma assisted molecular beam epitaxy using an AlN buffer layer [10]. Different pieces of the same wafer were implanted at 77 K with 700 keV In ions and fluences in the range $5\times10^{13} – 1\times10^{16}$ cm^{-2}. The RBS analysis was performed at room temperature with 2 MeV He ions, at a backscattering angle of 170°. The N - K edge NEXAFS measurements were conducted at the PM3 beamline of the storage ring BESSY-II of the Helmholtz Center Berlin for Materials and Energy. The beamline is equipped with a plane grating SX700 monochromator that offers a resolution of $\Delta E/E = 1\times10^{-4}$. The spectra were recorded in the fluorescence yield mode using a high purity Ge detector positioned on the horizontal plane at right angle to the beam. In order to avoid polarization effects, the angle of incidence was equal to the magic angle (55° to the sample surface) [7]. Under these recording conditions, the information depth of the fluorescence photons is approximately equal to 40 nm and therefore the NEXAFS spectra provide information only on the upper part of the implanted region.

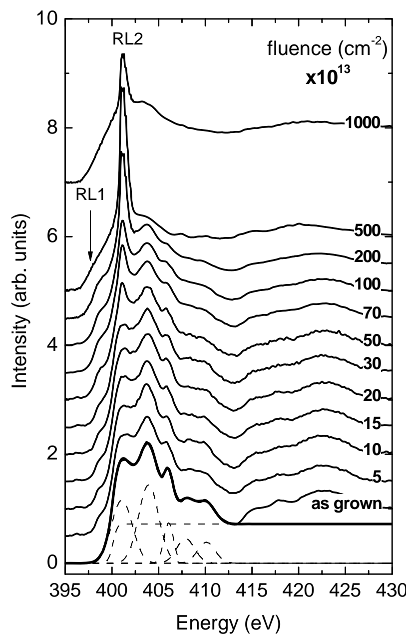

Figure 1. N - K edge NEXAFS spectra of the GaN samples implanted with various In ion fluences. RL1 and RL2 denote the peaks that appear after the implantation. A representative fitting of the spectrum from the as-grown sample is also included.

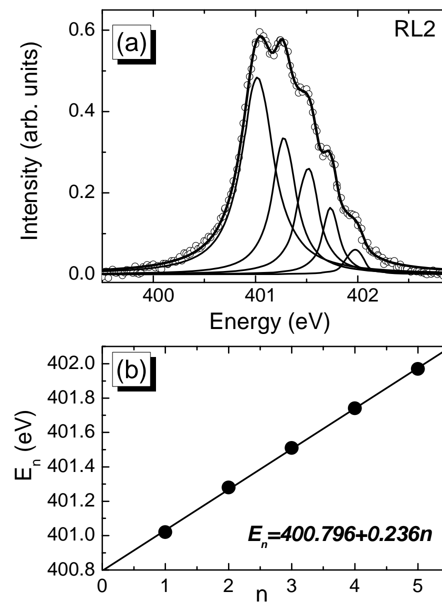

Figure 2. **(a)** Fitting of the fine structure of RL2 using n (n=1…5) Lorentzian functions; **(b)** linear fit of the energy position of each Lorentzian used to fit the RL2 *vs.* n.

3. Results and discussion

The N - K edge NEXAFS spectra of the GaN samples implanted with fluences $5\times10^{13} – 1\times10^{16}$ cm^{-2} are shown in figure 1. The spectra were subjected to linear background subtraction and normalization to the atomic limit (430 eV) [7]. The N - K edge NEXAFS spectra correspond to the partial density of empty states with N p-component distorted by the core-hole relaxation. The NEXAFS spectrum of the as-grown sample (fig. 1), which is crystalline with relatively low defect concentration, is characterized

by a number of peaks that correspond to maxima of the N p-partial density of states in the conduction band. Ion implantation affects the NEXAFS spectra in the following ways:

- It causes a broadening of the NEXAFS peaks as the implantation fluence increases (figure 1) and progressively smears out the fine structure of the NEXAFS spectrum. In the multiple - scattering view, as the implantation fluence increases and the static disorder is enhanced, the contribution of the single scattering paths of distant shells and/or multiple scattering paths in the NEXAFS spectra ceases.
- It causes the evolution of two resonance lines, designated as RL1 and RL2 which appear about 1.5 eV below and 1 eV above the absorption edge, respectively. The RL1 in the low-energy side of the absorption edge is attributed to the N split - interstitial defect [9]. This defect consists of two N atoms that occupy the same lattice site and introduces empty mid-gap states, i.e. about 1.6 eV below the conduction band. The RL2 appears after implantation with higher fluences compared to RL1 and its width is approximately constant. In addition to that, its energy position coincides with that of the 1s→π* transition in the N_2 molecule (401.0 eV). The fine structure of RL2 (recorded with a step of 0.02 eV) is shown clearly in Fig. 2(a). The RL2 is fitted using five Lorentzian functions with an energy difference of 236 meV with respect to each other, as shown in figure 2. The fine structure is attributed to the vibronic character of the transition since the electron transition 1s→π* is accompanied by a change of the vibrational quantum number of the N_2 molecule. A similar RL, attributed to 1s→π* transitions of N_2 trapped in semiconductors, has been detected in the spectra of bulk samples bombarded with low energy N_2^+[11] and in annealed N-doped ZnO [12].

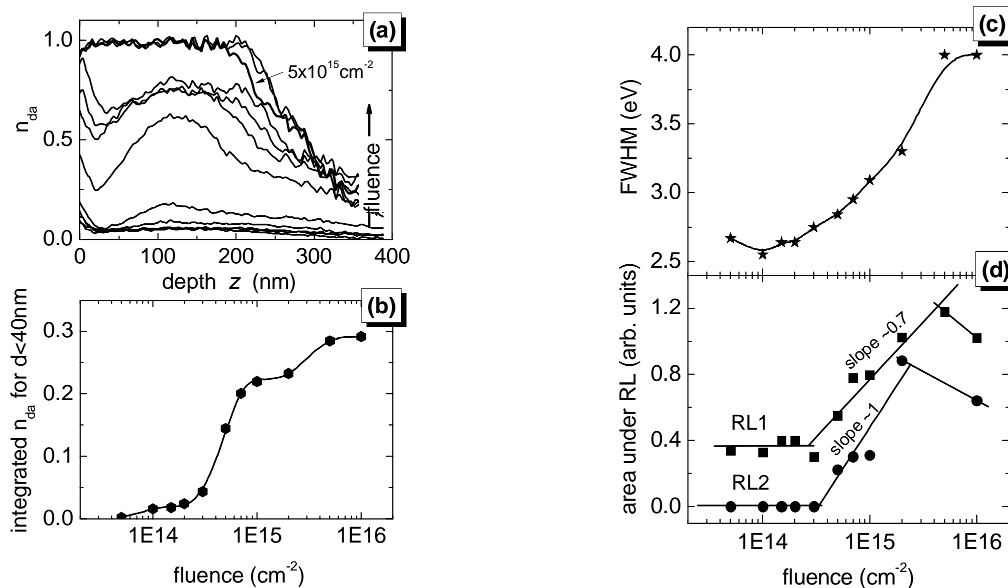

Figure 3. (a) Depth distribution of the relative concentration of displaced atoms (n_{da}) as determined by RBS; **(b)** area under the distributions shown in (a) integrated to the depth of 40 nm, **(c)** FWHM of the NEXAFS peak at 403.9eV and **(d)** area under the RL1 and RL2, as a function of the fluence.

In order to quantify the effects of ion implantation on the creation of defects, we resorted to fitting of the NEXAFS spectra shown in figure 1. The spectra were fitted using a sigmoidal, to simulate transitions to the continuum, and a number of Gaussians to simulate the NEXAFS peaks in the spectra of the as-grown and implanted samples (i.e. RL1 and RL2) [9]. A comparison of the NEXAFS and RBS results is shown in figure 3. More specifically, the depth distribution of the relative concentration of the displaced atoms, n_{da}, which is calculated from the RBS spectra using the DICADA code [13], is shown in figure 3(a). The values of n_{da} equal to 0 and 1 correspond to crystalline and amorphous material, respectively. The bimodal character of the distribution is characteristic of the strong dynamic

annealing of GaN [6]. The fluence of 5×10^{15} cm^{-2} which yields maximum n_{da}=1 (figure 3(a)) can be identified as the amorphization threshold. The area under the depth distribution curves within the information depth of measurements at the N-K-edge (i.e. 40 nm) is shown in figure 3(b). The full width at half maximum (FWHM) of the strongest NEXAFS peak at 403.9 eV varies with the fluence in a fashion similar to the defect concentration (figure 3(b)), as shown in figure 3(c). Finally a similar trend is observed for the area under the RL1 and RL2, as shown in figure 3(d). Regarding the RL's, the RL1 appears even after implantation with the fluence 5×10^{13} cm^{-2} where the defect concentration measured by RBS is approximately zero, showing that N split-interstitial defects are easily formed by the N atoms that are displaced from their lattice positions due to implantation. The threshold for the formation of N_2, most probably in the form of bubbles, is the fluence equal to 5×10^{14} cm^{-2}. Above this threshold, the RBS defect concentration as well as the concentration of the N split-interstitials and N_2 molecules increases abruptly. A significant decrease in the N-related defects is detected in the sample implanted with fluence equal to 1×10^{16} cm^{-2}, most probably due to its amorphous character. The split-interstitial defect and the N_2 bubbles anneal out at 800°C [14].

4. Conclusions

N - K NEXAFS spectroscopy identifies the formation of N split - interstitial defects in GaN samples implanted with 700 keV In ions. The split interstitial is formed even after implantation with a fluence as low as 5×10^{13} cm^{-2}. Implantation with a higher fluence ($\geq5\times10^{14}$ cm^{-2}) results to the formation of N_2 molecules whose signature in the NEXAFS spectra is a strong resonance line, with pronounced vibronic character, at 1 eV above the absorption edge. When the fluence exceeds 5×10^{14} cm^{-2}, the increase in the concentration of the N split-interstitial and N_2 defects detected by NEXAFS have a similar dependence with the increase of defect concentration according to RBS. In addition to that, the increase of the width of the NEXAFS peaks, as a function of the fluence, follows the same trend with the defect concentration measured by RBS.

Acknowledgements
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