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On the effect of ion implantation in the microstructure of GaN: an XAFS study

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Nitrogen *K*-edge EXAFS measurements are used to study the effect of N^+ and O^+ implantation in the microstructure of GaN. In the as-grown sample the central N atom is four-fold coordinated with 3.35 Ga atoms at the expected distance of 1.93Å, and 0.65 displaced to a distance longer by ~0.33Å. Implantation with either N or O ions enhances the distortion in the microstructure and the number of the displaced Ga atoms increases from 0.65 to 1. The enhancement of the distortion in the coordination number is attributed to the generation of excess N vacancies. In addition to that, implantation causes a reduction in the nearest neighbor distances by about 2% and an increase of the Debye-Waller factors.

Keywords: GaN; EXAFS; implantation; defects.

1. Introduction

GaN is a wide band gap semiconductor (E_g=3.34eV), which finds applications in optoelectronics for the fabrication of lasers and light emitting diodes which operate in the blue-green range of the visible spectrum (Nakamura, 1994). Due to the low reactivity of N with Ga, and the lack of bulk GaN for homoepitaxial growth, GaN is characterized from a high concentration of point and extended defects (mainly threading dislocations), that have detrimental effects on the performance of lasers. Among the native point defects the N vacancy (V_N), which is held responsible for the background n-type conductivity of undoped GaN films, has the lowest formation energy (Neugebauer, 1994). Other energetically favorable defects are V_{Ga}, the N antisite (N_{Ga}) and the N interstitial (N_i) (Neugebauer, 1994, Boguslawski, 1995, Corczyca, 1997).

The purpose of this work is to study the effect of N^+ and O^+ implantation in the microstructure of GaN using extended X-ray absorption fine structure (EXAFS). Since both V_N and O_N have been proposed as possible origins of the native n-type conductivity (Zopler, 1996), ion implantation (which is a common device processing step and permits good control over the implant concentration and profile), might provide a means to get a better understanding of the origin of n-type conductivity.

2. Growth conditions and experimental details

The nominally undoped GaN films were grown by metalorganic vapor phase epitaxy (MOVPE) on (0001)Al_2O_3 substrates. The epilayer is 1.2μm thick and has a background carrier concentration of $1x10^{17}cm^{-3}$. The GaN sample was implanted using N and O ions, with an energy of 70keV and a dose of $5x10^{14}$ cm^{-2}. The peak of the implant profile is at a depth of about 100nm from the surface. The x-ray absorption measurements were conducted under ultra high vacuum conditions (p<3.10^{-9} mbar) using light from the SX-700-I monochromator at the electron storage ring BESSY-I in Berlin. The EXAFS spectra were recorded in the energy range 370-970eV using a high purity Ge detector, which permits electronic isolation of the N and the O signals (Katsikini, 1997). The spectra were recorded at an angle of incidence equal to 55° to the sample surface, i.e. equal to the "magic angle" (Katsikini, 1997).

3. EXAFS analysis

Prior to analysis, the normalised spectra (with the electron yield current from a clean Si wafer) were corrected for self-absorption effects following the procedure described previously (Tröger, 1992, Katsikini, 1997). Then the spectra were subjected to subtraction of the atomic absorption using the AUTOBK program (Mustre de Leon, 1991). A model for hexagonal GaN (a=3.18Å, c=5.168Å) was constructed using the FEFF6 code (Mustre de Leon, 1991). The initial values for the Debye-Waller factors were calculated using the correlated Debye model (Sevillano, 1979) and a Debye temperature of 600K (Katsikini, 1997, 1998). The χ(k) spectra were fitted using paths, which correspond to the 3 nearest neighbor (nn) shells of N, i.e. 4 Ga atoms at 1.92Å, 12 N atoms at 3.18Å and 12 Ga atoms at 3.69Å. The fitting of the $k^3 \cdot \chi(k)$ spectra was done using the FEFFIT program (Mustre de Leon, 1991) by iteration of the coordination number, the nn distance and the Debye-Waller factor for each shell. The amplitude reduction factor and the energy shift (ΔE_0) were kept fixed at 0.93 and 3.74eV, respectively, for all the samples. Polarisation effects were not taken into account because the measurements were performed at an incidence angle equal to the "magic angle". The information depth in the energy range of interest is 40-70nm.

The χ(k) spectra and the corresponding Fourier Transforms (FT), in the k-range 4-12$Å^{-1}$, are shown in Fig. 1 (a) and (b), respectively. The experiment is shown in thin solid line and the fitting in thick solid line. The shoulder that appears in the FT's (indicated by an arrow) is not predicted by the hexagonal GaN model and indicates that the first nearest neighbors are not equidistant. In order to achieve good fitting one additional Ga path (the corresponding neighbor is hereafter called Ga') had to be included between the first and second nn shells which consist of Ga and N atoms, respectively (Katsikini, 1997). An additional Ga path was also necessary in the next higher shell consisting of Ga atoms (3rd shell in the model). The analysis results for the coordination numbers, the nn distances and the Debye-Waller factors for the three first nn shells are listed in Table 1.

4. Results and discussion

In the as-grown sample the N atom is four-fold coordinated with 3.35 Ga atoms at the expected distance of 1.93Å and 0.65 Ga atoms at 2.26Å, i.e. displaced by 0.33Å (~15% of the equilibrium bond-length). This result is in agreement with previously reported results for undoped GaN grown by other epitaxial techniques (Katsikini, 1997) and Mg-doped GaN (Katsikini,

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1998). This distortion in the microstructure has been attributed to nitrogen vacancies V_N (Katsikini, 1997, 1998), which according to the calculations of Neugebauer (1994), have the lowest formation energy in GaN. In the immediate neighborhood of a V_N the four Ga atoms surrounding the vacancy interact strongly (metallic-like interaction) and that leads to an elongation of 12 Ga-N bonds around the V_N.

Table 1

Nearest neighbor shell parameters for the sample in the as-grown state and after N and the O ion implantation (denoted as GaN, GaN:N and GaN:O, respectively): coordination numbers ($N^{(i)}$), nn distances ($R^{(i)}$), Debye-Waller factors ($A^{(i)}$) for the as-grown, the GaN. The error bars were determined using two different spline functions for the subtraction of the atomic background. $N^{(1')}$, $R^{(1')}$, $A^{(1')}$ and $N^{(3'')}$, $R^{(3'')}$, $A^{(3'')}$ are the corresponding parameters for the additional paths used for the fitting after the 1st and the 3rd nn shell of Ga atoms respectively.

shell parameters		GaN	GaN:N	GaN:O
	$N^{(1)}_{Ga}\pm10\%$	3.35	2.93	3.08
1st shell	$R^{(1)}_{N\text{-}Ga}\pm0.01$ (Å)	1.93	1.89	1.89
(Ga)	$A^{(1)}_{Ga}\pm10\%$ (Å^2)	$6.9\cdot10^{-3}$	$7.2\cdot10^{-3}$	$7.8\cdot10^{-3}$
	$N^{(1')}_{Ga}\pm10\%$	0.65	1.07	0.92
additional	$R^{(1')}_{N\text{-}Ga}\pm0.01$ (Å)	2.26	2.20	2.18
shell (Ga′)	$A^{(1')}_{Ga}\pm10\%$ (Å^2)	$7.1\cdot10^{-3}$	$7.5\cdot10^{-3}$	$8.1\cdot10^{-3}$
	$N^{(2)}_{N}\pm15\%$	12.0	12.0	12.0
2nd shell (N)	$R^{(2)}_{N\text{-}N}\pm0.03$ (Å)	3.16	3.07	3.08
	$A^{(2)}_{N}\pm15\%$ (Å^2)	$8.7\cdot10^{-3}$	$1.3\cdot10^{-2}$	$1.2\cdot10^{-2}$
	$N^{(3)}_{Ga}\pm25\%$	7.36	6.08	6.71
3rd shell	$R^{(3)}_{N\text{-}Ga}\pm0.03$ (Å)	3.71	3.67	3.64
(Ga)	$A^{(3)}_{Ga}\pm30\%$ (Å^2)	$5.7\cdot10^{-3}$	$1.4\cdot10^{-2}$	$1.4\cdot10^{-2}$
	$N^{(3'')}_{Ga''}\pm25\%$	4.63	5.92	5.29
additional	$R^{(3'')}_{N\text{-}Ga''}\pm0.03$ (Å)	3.91	3.97	3.98
shell (Ga′′)	$A^{(3'')}_{Ga''}\pm30\%$ (Å^2)	$6.3\cdot10^{-3}$	$1.5\cdot10^{-2}$	$1.5\cdot10^{-2}$

The effects of either N^+ or O^+ implantation on the microstructure of GaN are indistinguishable. Implantation with either element enhances the distortion in the microstructure and the main effects in the nn shell-parameters are the following:

i) The distances in the 1st and 2nd nn shells (consisting of Ga and N atoms, respectively) are reduced by about 1.7% and 2.5% respectively. This reduction corresponds to a reduction of the volume of the unit cell by about 7%. Such a reduction in the unit cell volume could be attributed to the implantation-induced generation of vacancies (V_N or V_{Ga}) (Lagerstedt, 1979).

ii) The number of the displaced Ga atoms increases from 0.65±0.06 to 1±0.1. According to the model proposed for the distortion in the microstructure of GaN, an increase of the number of the displaced Ga atoms could correspond to an increase of the V_N concentration.

iii) The Debye-Waller factors increase after the implantation by ~5% in the 1st shell (Ga atoms), by ~50% in the 2nd shell (N atoms) and by ~150% in the 3rd shell (Ga atoms). This is an indication of defect formation and/or partial-amorphization (increase of the static disorder). It should be pointed out that transmission electron microscopy results (Lioutas 1998) reveal that the implantation has only

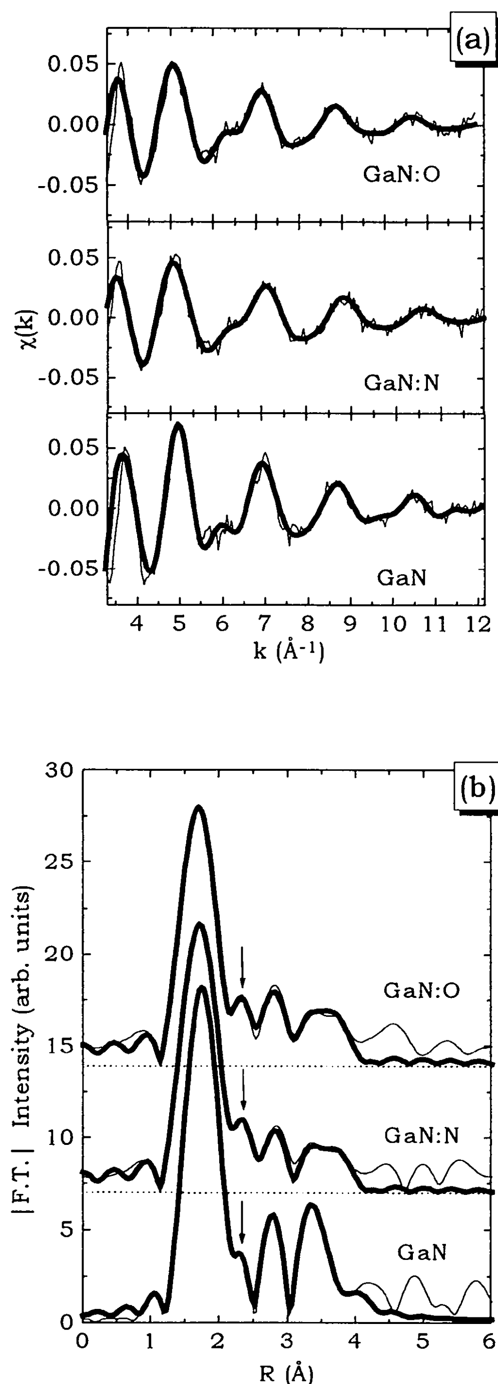

Figure 1

(a) χ(k) spectra of the GaN film prior and after N^+ and O^+ implantation.

(b) The corresponding Fourier Transforms. The experimental curve and the fitting are shown in thin and thick solid lines, respectively. The arrow in the FTs indicates the additional Ga path.

increased the dislocation density in the epilayer while the film retains its crystalline nature.

5. Conclusions

In conclusion, evidence is provided that the distortion in the microstructure of GaN is related to the vacancy population. Ion implantation creates a sufficient concentration of V_N to cause a reduction of the unit cell volume by approximately 7%. The increase in the number of displaced Ga atoms along with the fact that the coordination remains tetrahedral, indicates that the V_N population exceeds by far that of V_{Ga}. Indeed, from mass considerations it would be expected that the N^+ and O^+ implantation would result in a higher V_N population. Finally, the increased values of the DW factor are compatible with the implantation-induced disorder.

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