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Nitrogen *K*-edge EXAFS measurements on Mg- and Si-doped GaN

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EXAFS measurements at the N *K*-edge are used to study the microstructure of n- and p-type GaN doped with Si and Mg, respectively. In undoped and Mg-doped GaN the nitrogen atom is four-fold coordinated with n (where 2.9<n<3.3) Ga atoms in the expected distance of 1.93Å and 4-n at a distance longer by ~0.28Å. Such a distortion in the nearest neighbor (nn) distances is not detected in GaN:Si where the nitrogen atom is found undercoordinated with 3.3 instead of 4 Ga atoms. These results are discussed in relation to the presence of N and Ga vacancies, which exist in GaN samples. Furthermore, the effect of native defects on the lattice constants is also discussed.

Keywords: GaN; doping; EXAFS; defects; microstructure.

1. Introduction

GaN is a wide-band gap semiconductor which finds applications in a wide range of opto- and microelectronic devices including emitters, detectors and lasers which operate in the blue-green range of the spectrum (Akasaki & Amano 1998). Epitaxially grown GaN films are characterised by high densities of point and extended defects which are held responsible for the high background n-type conductivity in undoped GaN and the yellow luminescence (~2.2eV) (Perlin *et al.*, 1995, Neugebauer & Van de Walle, 1996). Among the native defects in GaN, the nitrogen vacancy (V_N) has the lowest formation energy (Neugebauer & Van de Walle, 1994). Here we apply EXAFS in order to study the effect of doping on the native defect population and the local microstructure around the N atom, in epitaxially grown GaN.

2. Growth conditions and experimental details

The samples were grown by electron cyclotron resonance molecular beam epitaxy on (0001) Al_2O_3 (GaN179, GaN441, GaN449 and GaN407) and (111) Si (GaN67) substrates. The epilayers were 1-1.7μm thick while Si and Mg were used as the n- and p-dopands, respectively. The net carrier concentration in the Mg-doped samples GaN441 and GaN449 is $1\times10^{17}cm^{-3}$ and $5\times10^{17}cm^{-3}$, respectively. In the Si-doped sample GaN407 the carrier concentration is $1.57\times10^{18}cm^{-3}$ (the activation energy of the activation of the Si and Mg dopants is 27meV and 170meV, respectively). The samples GaN179 and the GaN67 samples are undoped. Details of the growth conditions and other characterisation results have been reported previously (Moustakas & Molnar, 1993). The N *K*-edge EXAFS measurements were conducted under UHV conditions ($p<3\times10^{-9}$mbar) using the SX-700-I monochromator at the storage ring BESSY-I in Berlin. The EXAFS spectra were recorded in the energy range of 370-970eV using a high purity Ge detector (fluorescence yield).

3. Results and discussion

Prior to the analysis, the EXAFS spectra were normalised to the flux of the monochromator by division with the electron yield spectrum from a clean Si wafer. The normalised EXAFS spectra were subjected to subtraction of the atomic absorption using the AUTOBK program (Mustre de Leon *et al.*, 1991). The spectra were corrected for self-absorption effects in the k space using the procedure described previously (Katsikini *et al.*, 1997). A model for hexagonal GaN (a=3.18Å, c=5.168Å) was constructed using the FEFF6 code (Mustre de Leon *et al.*, 1991). The initial values for the Debye-Waller (DW) factors were calculated using the correlated Debye model (Sevillano *et al.*, 1979) and a Debye temperature of 600K (Katsikini *et al.*, 1997).

Table 1
EXAFS analysis results for the coordination numbers (N_i), the nn distances (R_i) and the Debye-Waller factors (A_i). The error bars were determined using different spline functions for the subtraction of the atomic background. The samples GaN67 and GaN179 are undoped, GaN441 and GaN449 are p-type and GaN407 is n-type.

		sample name				
shell parameters		GaN67	GaN179	GaN407	GaN441	GaN449
1st shell (Ga)	N_{Ga}±10%	2.9	2.9	3.3	3.3	3.2
	R_{N-Ga}±0.01 (Å)	1.91	1.91	1.93	1.90	1.90
	A_{Ga}±10% (Å^2)	$5.2\cdot10^{-3}$	$5.6\cdot10^{-3}$	$6.9\cdot10^{-3}$	$7.1\cdot10^{-3}$	$7.1\cdot10^{-3}$
ad. shell (Ga')	N_{Ga}±10%	1.1	1.1	-	0.7	0.8
	R_{N-Ga}±0.01 (Å)	2.19	2.19	-	2.18	2.18
	A_{Ga}±10% (Å^2)	$5.5\cdot10^{-3}$	$5.9\cdot10^{-3}$	-	$7.4\cdot10^{-3}$	$7.3\cdot10^{-3}$
2nd shell (N)	N_N±15%	13.0	13.0	12.0	12.0	12.0
	R_{N-N}±0.03 (Å)	3.13	3.12	3.16	3.10	3.12
	A_N±15% (Å^2)	$1.1\cdot10^{-2}$	$1.1\cdot10^{-2}$	$1.1\cdot10^{-2}$	$7.1\cdot10^{-3}$	$7.0\cdot10^{-3}$

The $\chi(k)$ spectra were fitted using paths which correspond to the 3 nearest neighbor (nn) shells of N, i.e. four Ga atoms at 1.92Å, 12 N atoms at 3.18Å and 12 Ga atoms at 3.69Å. The fitting was done using the FEFFIT program (Mustre de Leon *et al.*, 1991) by iteration of the coordination number, the nn distance and the DW factor for each shell. The amplitude reduction factor was kept fixed at 0.93 for all the samples and the energy shift (ΔE_0) was iterated and took values 5±2eV.

Polarisation effects were not taken into account because the measurements were performed at an incidence angle equal to the "magic angle", i.e. at 54.7° to the sample surface (Katsikini *et al.*, 1997).

The $\chi(k)$ spectra weighted by k^3 are shown in Fig. 1 and the corresponding Fourier Transforms (FT), in the k-range 4-12Å^{-1}, are shown in Fig. 2 (the experiment is shown in thin solid line and the fitting in thick solid line). The shoulder in the FT's of the undoped samples GaN179 and GaN67 and the Mg-doped GaN441 and GaN449, indicated by the arrow, is not predicted from the hexagonal GaN model and indicates that the first nearest neighbours are not at the same N-Ga distance. 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 consisting of Ga and N atoms, respectively (Katsikini *et al.*, 1997). The additional Ga path was also necessary for the fitting of the next higher shell consisting of Ga atoms. The introduction of the additional Ga paths improves the quality of the fitting, as indicated by the simultaneous reduction of the χ^2 and χ^2_v factors, calculated within the FEFFIT (Mustre de Leon *et al.*, 1991). 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. For the undoped and the Mg doped samples the N atom is four-fold coordinated with three Ga atoms at the expected distance of 1.90-1.91Å and 1 Ga atom at 2.18-2.19Å, i.e. displaced by 0.28Å (~15% of the equilibrium bond-length). Contrary to the undoped or Mg-doped samples, the n-type sample GaN407 (doped with Si) does not show a distortion in the nn distances but it shows an undercoordination of the N atom, i.e. N_{Ga} is found to be 3.3 instead of 4.

The distortion of the microstructure of undoped GaN, identified by EXAFS, has been attributed to thermal strain (between the epilayer and the substrate) and/or inhomogeneous strain due to the presence of native defects (Katsikini *et al.*, 1997). According to the calculations of Neugebauer & Van de Walle (1994), local lattice distortion is expected around V_N. Under p-type doping and intrinsic conditions, the formation of V_N is favoured, while under n-type doping conditions V_{Ga} are more easily created. When a V_N is formed, and due to the small ionic radius of the N atom (0.74Å), the Ga atoms which surround the vacancy can interact strongly with each other. This interaction is metallic-like (the Ga-Ga distance approaches that in the Ga metal, i.e. it is about 2.5Å) and can induce distortions in the local microstructure around the N atom. Since V_N are present in large concentrations in undoped or p-type doped films, and taking into account that one V_N distorts 12 N-Ga distances in its neighbourhood, the local distortion due to V_N could be detectable as a distortion in the nn distances. Indeed this is observed in the undoped and Mg doped samples. In the case of n-type doped GaN:Si, where the concentration of V_N is expected to be smaller (Neugebauer & Van de Walle, 1994), the distortion in the first nn shell is not

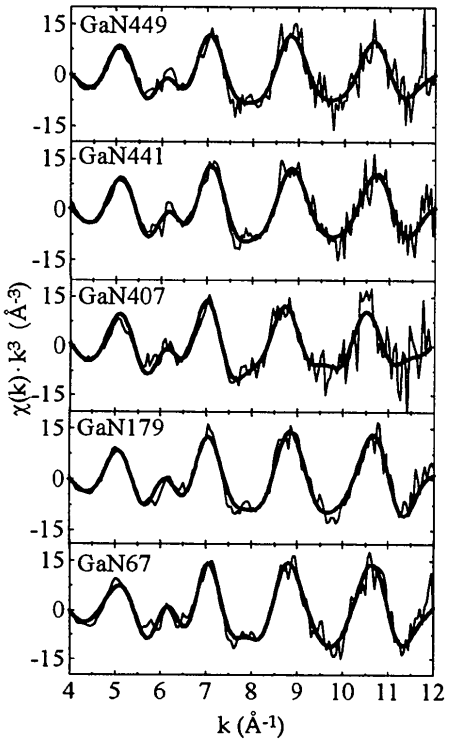

Figure 1
The $k^3\chi(k)$ spectra from the five samples that have been examined. The spectra and the fitting are shown in thin and thick lines, respectively.

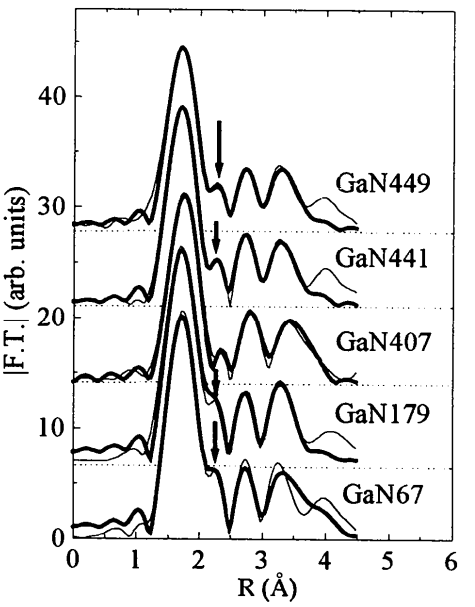

Figure 2
The Fourier transforms of the $k^3\chi(k)$ spectra shown in Fig.1. The additional Ga shell in the spectra of GaN67, GaN179, GaN441 and GaN449 is indicated by an arrow.

detected. The detected undercoordination in the 1st nn shell in GaN:Si is an indication of the presence of V_{Ga}, as it would be expected for n-type doped GaN (Neugebauer & Van de Walle, 1994), and/or nitrogen antisite defects. Even though lattice relaxation around Ga vacancies has also been theoretically predicted (resulting in a 5% increase of the second nn distance) (Neugebauer & Van de Walle, 1996), it is not detectable by EXAFS for several reasons including the limited interaction among the N atoms surrounding the V_{Ga} and the fact that N is a 2nd nn and "lighter" backscatterer than Ga.

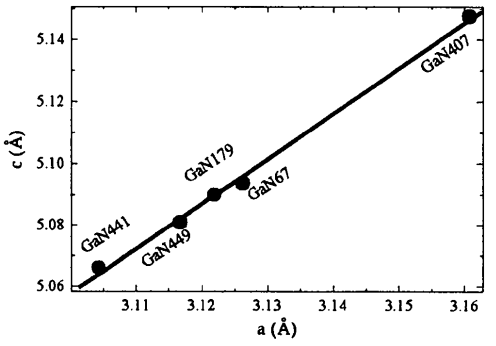

Figure 3
The lattice constants of the five samples. The c/a ratio remains constant and equal to 1.63.

The lattice constants of the samples can be calculated using the nn distances and the following formulas: $a=R_{N-N} \pm 0.025$Å and $c=(8/3)\cdot R_{N-Ga} \pm 0.01$Å. Although the values of a and c in the under-study MBE-grown samples vary by about 1.5%, the ratio of the lattice constants, c/a, remains constant and equal to 1.63, as shown in Fig.3. This result indicates that the deviation of the lattice parameters from the expected values is a non unit-cell volume-conserving one. However, the samples retain their wurtzite structure, despite the deviation in the values of c and a. Our results indicate the c and a vary with doping and the concentration of V_N, in agreement with the X-ray diffraction results of Lagerstedt & Monemar (1979).

4. Conclusions

In conclusion, it is demonstrated that EXAFS can identify local distortions in the microstructure of GaN due to the presence of defects. A distortion in the local microstructure is detected in the undoped and Mg-doped GaN where one out of the four nn to the N atom is found at a distance longer than expected by 15%. This distortion is attributed to the strong interaction between the Ga atoms surrounding nitrogen vacancies. The distortion in the nn distances is not detected in the Si-doped GaN where an undercoordination is detected in the 1st nn shell. This undercoordination could be attributed to the presence of V_{Ga} and/or nitrogen antisite defects. Finally, among the various samples the Si doped sample had lattice constants close to the expected values. All the other samples had smaller lattice constants but the ratio c/a remained constant and equal to 1.63. This result indicates that the deviation of the lattice parameters from the expected values, mainly due to the growth conditions, is a non unit-cell-volume conserving one.

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