Verification of a distortion in the microstructure of GaN detected by EXAFS using *ab initio* density functional theory calculations

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X-ray absorption fine structure (XAFS) measurements on a series of epitaxially grown GaN samples have shown a distortion in the microstructure of GaN. More specifically the central N atom is 4-fold coordinated but the four Ga atoms are not equidistant. It has been shown that 2.9 to 3.5 of them (depending on the growth conditions) are found in the expected from XRD distance of 1.94 $\mathring{A}$ and the remaining are at a distance longer by approximately 15%. Second derivative calculation of the conformation energy using the Density Functional Theory (DFT) is used to investigate if the symmetric GaN cluster as given by XRD is the most energetically favorable configuration and if not which distorted structure corresponds to the most energetically favorable one. A very good agreement between DFT results and experimental XAFS spectra has been found. Generalization this technique to other dislocated clusters is also discussed.

Keywords: EXAFS; Density Functional Theory; GaN.

1. Introduction

Gallium Nitride (GaN) is a wide band gap semiconductor which finds applications in optoelectronics and microelectronics. The ternary alloys $Al_xGa_{1-x}N$ and $In_yGa_{1-y}N$ permit bandgap engineering and cover a spectrum from yellow to ultraviolet. Although GaN has been used for the fabrication of devices, it is characterized by a high concentration of point and extended defects which are held responsible for the parasitic yellow luminescence and the native n-type conductivity. GaN crystallizes in the cubic (zincblende) and the more stable hexagonal (wurtzite) structures. The microstructure of the cubic and the hexagonal polytypes is similar up to the 3rd nearest neighbor (nn) and the two polytypes differ only in the stacking sequence of the planes.

Extended X-ray absorption fine structure (EXAFS) measurements at the N-K-edge on a series of epitaxially grown GaN samples have identified a distortion in the microstructure of GaN (Katsikini *et al.*, 1999a, Katsikini *et al.*, 1997). The central nitrogen atom is 4-fold coordinated but the four gallium atoms are not equidistant. Among them 2.9 – 3.5 (depending on the growth conditions) are found at the expected distance of 1.94 $\mathring{A}$ while the remaining atoms are at a distance longer by 15%. EXAFS measurements at the Ga-K-edge verify the presence of the distortion (Katsikini *et al.*, 1999b).

In order to confirm the EXAFS results we apply a self-consistent (SCF) *ab initio* quantum chemistry method which among other pieces of information will provide normal mode eigenfrequencies for a given cluster. The Density Functional Theory (DFT) (Parr, R.G. & Yang W., 1989.) is an *ab-initio* method which was chosen due to its accuracy and speed [1]. For a given geometry all normal mode frequencies must be positive, else the given structure does not represent a stable state (Goddard W., 1998). A negative frequency, present in the normal mode spectrum, means that the second energy derivative is negative i.e. the system has converged to an unstable saddle point and not to an energy minimum. In non-crystalline structures this problem could be overcome by geometry optimization. But in crystalline structures no geometry optimization is performed because this will lead to a cluster relaxation, and so using the XRD atomic positions no negative frequencies should be present in the spectrum. As it follows in case of the hexagonal GaN negative frequencies were present in the spectrum if the XRD atomic positions were used.

The use of DFT method can also provide possible distorted structures that correspond to an energetically favorable configuration. As it has been mentioned before, in case of crystalline structures ordinary geometry optimization will lead to cluster relaxation. This happens because in the real case a crystal is an infinite lattice whereas in the molecular modeling programs only a part of it will be used thus creating the so called edge atoms. Edge atoms will see other atoms only from certain directions and vacuum from others. Since this is unrealistic, edge atoms must be locked to fixed positions. If CPU resources are fairly enough then a large cluster of the crystal under investigation could be built and all non-edge atoms could be let free to move i.e. geometry optimization of internal atoms could be performed if edge atoms stay fixed just to mimic the periodic boundary conditions. Alternatives to this CPU costly method is the use of radial distances from EXAFS and manually change the angles until all normal mode frequencies are positive.

2. Sample growth and experimental details

The distortion in the microstructure has been observed in a series of samples (cubic, hexagonal, mixed-phase) doped and undoped as well as implanted with N and O. In the present study we shall focus on hexagonal Si doped GaN grown by metalorganic vapor phase epitaxy on (0001) Al_2O_3, at a temperature of $1050°C$. The N K-edge EXAFS measurements were conducted under UHV conditions ($p < 3 \times 10^{-9} mbar$) using the SX-700-I monochromator at the storage ring BESSY-II in Berlin. The EXAFS spectra were recorded in the energy range of 370-970 eV at an angle of $55°$ from the sample surface using a high purity Ge detector (fluorescence yield). The Ga-K-edge EXAFS measurements were conducted at the X1 beamline (double Si-crystal monochromator) in HASYLAB, Hamburg. The EXAFS spectra were recorded in the energy range 10200-11350 eV and the fluorescence photons were detected using a $NaI(Tl)$ scintillation detector. The angle of incidence was $45°$ to the sample surface and the detection angle was $90°$. Prior to analysis the spectra were normalized to the primary beam current, which was measured using an ionization chamber, positioned before the sample.

3. EXAFS characterization

The EXAFS spectra were subjected to background subtraction using the AUTOBK program (Mustre de Leon et al., 1991). The

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[1]DFT in the LDA case scales as N^3 where N is number of basis set used. DFT accuracy, depending on the functional used can be as much as 99% of the experimental normal mode frequency value.

$\chi(k)$ spectra were fitted using the model for hexagonal GaN constructed with the program FEFF8 (Mustre de Leon et al., 1991). The nearest neigbohr distances and coordination numbers are the same if N or Ga atom is considered as the central absorbing atom but the Ga and N neighbors alternate. The $\chi(k)$ spectra recorded at the N- and Ga-K-edge and the corresponding Fourier Transform are shown in Fig. 1. The experimental curve and the fitting are shown in thin and thick solid line respectively. The fitting results for measurements at the N and Ga -K edge are listed in Table 1.

Table 1
Fitting parameters for the N- and Ga-K edge EXAFS characterization

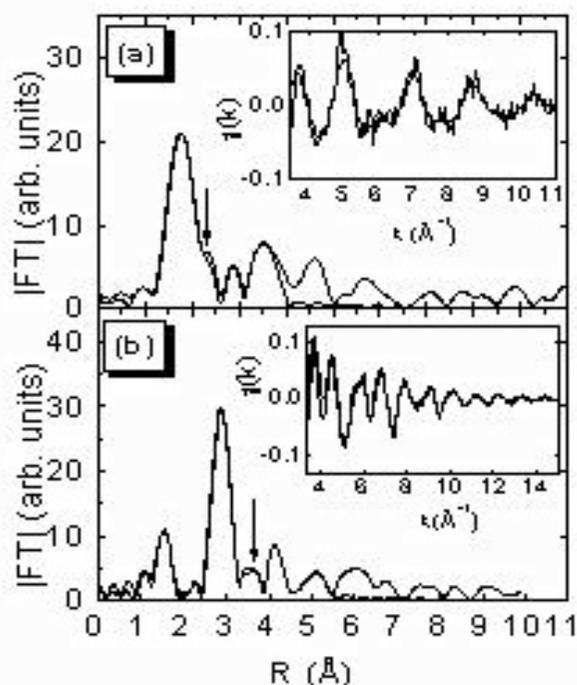| Edge	Type	N	R(Å)	$\sigma^2(\text{Å}^2 \times 10^{-3})$
N-K-edge $(300K)$	Ga	3.3	1.93	4.0
	Ga'	0.7	2.16	8.07
	N	12.0	3.15	5.1
	Ga	10.0	3.72	10.0
Ga-K-edge $(200K)$	N	4.0	1.93	5.0
	Ga	9.6	3.19	5.9
	N	10.0	3.71	16.3
	Ga''	2.4	4.05	8.3

Figure 1
Fourier transform of the $\chi(k)$ spectrum shown in the inset recorded at the *(a)* N-K-edge and *(b)* Ga-K-edge. The fitting and the experimental curve are shown in thick and thin solid line, respectively. The arrows indicate the additional paths used for the fitting.

At the N-K-edge the N atom is found 4-fold coordinated with 3.3 Ga atoms at the expected distance of 1.93Å and 0.9 at distance longer by 0.19 Å. The 2nd and the 3rd nn shells, consisting of N and Ga atoms, respectively, are found at the expected distances. At the Ga-K-edge the distortion is detected in the 2nd nn shell which is split in two: 9.6 Ga atoms are found at the expected

distance of 3.19 Å and the rest 2 at a distance longer by 0.83 Å. The additional Ga path is denoted as Ga' in the case of the N edge and as Ga" in the case of Ga edge. By studying about 20 samples of different symmetry, grown using different techniques, either doped or undoped the following range of nn distances was found: $r_{N-Ga} = 1.93 - 1.95\text{Å}$, $r_{Ga-Ga} = 3.18 - 3.19\text{Å}$, $r_{N-Ga'} = 2.16 - 2.27\text{Å}$ and $r_{Ga-Ga''} = 3.98 - 4.10\text{Å}$. The additional Ga paths used for the fitting are marked with an arrow in Fig 1 (a) and (b). Possible splitting in the nn shells that consist of N atoms is more difficult to be detected due to the fact that N is a light backscatterer.

4. Confirmation of GaN distortion

Distortion on the hexagonal GaN was also confirmed using DFT under both the Local Spin Density (LSD) (Vosko, S.H, Wilk., L., and Nusair M., 1980) and Perdew-Wang 92 (PW92) (Perdew, J.P., and Wang, Y., 1992) functionals. The atomic basis set used in the calculations was double-zeta (DZ) type. The commercial software used was Unichem/DGAUSS 4.1 by Oxford Molecular Group and the hardware an ORIGIN 200 dual tower by Silicon Graphics with four R1200 CPUs.

We first performed full normal mode analysis on the small tetrahedron Ga_4N using its corresponding XRD coordinates. As it can be seen in Table 2 a strong saddle point at -556.73 cm^{-1} for LSD and -568.74 cm^{-1} for PW92 appears in the spectrum. Although small saddle points about $10 - 20$ cm^{-1} might be present in the spectrum of especially biological samples that involve organic rings and are flexible to rotate along a major axis, [2] large saddle points especially in crystalline structures that they are locked to the XRD positions denote that the corresponding cluster has a wrong structure. Even by increasing the cluster size and adding 12 more N and repeat calculation its is found that the strong saddle point was split in smaller but still negative frequencies. Therefore the presence of the saddle points is not a size-cluster effect. The lowest spin multiplicity has been chosen, i.e. doublet state for all clusters. [3]

Therefore in order to test if XRD coordinates are valid for the local structure we just have to built a very small cluster and check if all normal mode frequencies are positive.

Table 2
Negative Frequencies for various GaN clusters. Spin multiplicity is 2.

Cluster	Energy	Saddle Points
	Hartrees	cm^{-1}
Ga_4N^1	-7740.1578	-556.73,-70.64,-64.10
[2]	-7740.1054	-568.74,-70.51,-63.99
$Ga_4N_{13}^1$	-8390.4625	-115.87,-113.12,-109.66,-95,
		-90.1,-87.24,-68.82,-51
[2]	-8390.3823	-116.36,-113.78,-110.31,-95.47,
		-90.62,-87.98,-69.55,-52.60

[1] LDA, [2] PW92

5. Possible distorted GaN structures

A possible distorted cluster was determined by using the tetrahedron under LSD functional and constraining the radial distances from the central N atom. These distances were constrained to $r_{N-Ga} = 1.95\text{Å}$ for the three and $r_{N-Ga} = 2.25\text{Å}$ for the

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[2]These and are due to numerical errors.

[3]Although spin optimization is a more general technique to determine the spin that corresponds to ground state of the particular crystalline cluster, in this case was not necessary. This is due to the fact that either of the clusters were constructed symmetricallty from the central N atom.

fourth Ga atom. Among the 6 Ga-Ga bonds which are formed in a tetrahedron one is kept equal to $r_{Ga-Ga} = 3.98\mathring{A}$. We found that ground state energy for a possible structure with no negative frequencies should be no less than -7740.1678 hartrees (LSD). If the energy is less than this number saddle points start to appear in the spectrum. For this energy it was found that $r_{Ga-Ga} = 3.096\mathring{A}$ for two of these and $r_{Ga-Ga} = 3.14\mathring{A}$ for the next two and $r_{Ga-Ga} = 3.19\mathring{A}$ for the last one. This is with agreement with EXAFS data which show 9.6 Ga atoms at a distance of $3.19\mathring{A}$ and 2.4 at a distance of $4.05\mathring{A}$. It should be taken into account that in a perfect crystal the second nn shell of Ga consists of 12 Ga atoms. The Ga-Ga distance $r_{Ga-Ga} = 3.096\mathring{A}$ is difficult to be discriminated from $r_{Ga-Ga} = 3.14\mathring{A}$ using EXAFS for reasons explained before.
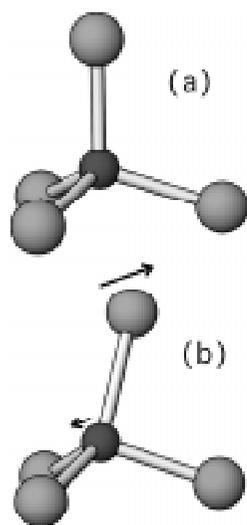

Figure 2
(a) Symmetric vs (b) Distorted GaN tetrahedron constructed on the basis of DFT calculations.

6. Conclusions

Second derivative conformational energy calculations on GaN clusters using DFT confirm experimental EXAFS data that the local environment of N in GaN is distorted, i.e. it is not the predicted by XRD measurements. Using second derivatives again we try to determine possible structures such as no saddle points will appear in the spectrum. Generalization of this technique to other clusters is under investigation.

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