J. Synchrotron Rad. (1999). **6**, 561–563

Gallium *K*-edge EXAFS measurements on cubic and hexagonal GaN

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The microstructure of undoped cubic and hexagonal GaN films is studied using temperature dependent Ga *K*-edge EXAFS measurements (10K-290K). The microstructure around the Ga atom is distorted due to a splitting of the second nearest neighbor shell, which consists of Ga atoms. This splitting results in an additional Ga path at a distance longer than expected by 0.8±0.05 Å and is attributed to local lattice relaxation around nitrogen vacancies. From the temperature dependence of the DW factors for the 2nd nearest neighbor shell of Ga, the Einstein temperature is equal to 318±25K.

Keywords: GaN; EXAFS; Einstein temperature; binary semiconductors.

1. Introduction

GaN is a wide band gap semiconductor, which finds applications in micro- and optoelectronics for the construction of emitters and detectors (Akasaki & Amano, 1998). It exists in two polytypes, the cubic (zincblende) and the hexagonal (wurtzite) which is the most easily stabilized. GaN is characterized from high concentrations of point defects such as vacancies, nitrogen antisites and interstitials (Neugebauer & Van de Walle, 1994) as well as extended defects, i.e. dislocations and stacking faults. The stacking faults can promote growth of mixed-phase crystals in which the cubic and the hexagonal polytypes coexist. According to N *K*-edge EXAFS measurements reported previously, the microstructure around the N atom is distorted due to the presence of native defects, mainly nitrogen and gallium vacancies (V_N, V_{Ga}, respectively) (Katsikini *et al.*, 1997, 1998). In the present work, the microstructure of GaN is studied using EXAFS measurements at the Ga *K*-edge.

2. Sample growth and experimental details

The under study samples, GaN179 (hexagonal) and GaN57 (cubic) were 1.6μm thick and were grown at 600°C on (0001)Al_2O_3 and (100)Si substrates, respectively, by electron cyclotron resonance molecular beam epitaxy. Details on the growth conditions have been reported previously (Moustakas & Molnar, 1993). The EXAFS measurements were conducted at the A1 and X1 beamlines (double Si-crystal monochromator) in HASYLAB, Hamburg. The EXAFS spectra were recorded in the energy range 10,200-11,350eV and the fluorescence photons were detected using a NaI(Tl) scintillation detector. The measurements were conducted in the temperature range 10-300K using a He cryostat. The angle of incidence θ was 45° or 35° to the sample surface and the detection angle was 90° -θ. Prior to analysis the spectra were normalized to the primary beam current, which was measured using an ionization chamber, positioned before the sample.

3. Results and discussion

The EXAFS spectra were subjected to background subtraction using the AUTOBK program (Mustre de Leon *et al.*, 1991). The χ(k) spectra were fitted using the model for hexagonal GaN (a=3.18Å, c=5.168Å) constructed with the program FEFF6 (Mustre de Leon *et al.*, 1991). According to the model, the three nearest neighboring (nn) shells consist of 4 N atoms at 1.92Å, 12 Ga atoms at 3.18Å and 12 N atoms at 3.69Å. The initial values for the Debye-Waller factors were calculated using the correlated Debye model (Sevillano *et al.*, 1979) and a Debye temperature of 600K (Katsikini, 1997). The χ(k) spectra, weighted by k^3, were fitted using the FEFFIT program (Mustre de Leon *et al.*, 1991) by iteration of the coordination number, the nn distance and the Debye-Waller factor for each shell. The amplitude reduction factor was kept fixed at 0.98 while the energy shift (ΔE_0) was iterated and took values between 5 and 5.55eV.

The χ(k) spectrum of the hexagonal sample recorded at T=200K is shown in Fig. 1(a) and the corresponding FT, in the k-range 3.6-12.55$Å^{-1}$, in Fig. 1(b). The experimental curve and the fitting are shown in thin and thick solid lines, respectively. The arrows in Fig. 1 (b) indicate the paths used for the fitting. The EXAFS oscillations extend up to k=16$Å^{-1}$ but the use of the k-range up to 12.55$Å^{-1}$ enhances the N contribution in the FT relative to that of Ga. The Ga• path is an additional Ga path at R=4Å (not predicted by the model) which is necessary to improve the quality of the fitting in both the k- and the R-spaces (in the range: 3.7-4.1Å).

The fitting results are listed in Table 1. The errors were determined using two different spline functions for the subtraction of the atomic background. The coordination numbers for the hexagonal sample are corrected for polarization effects.

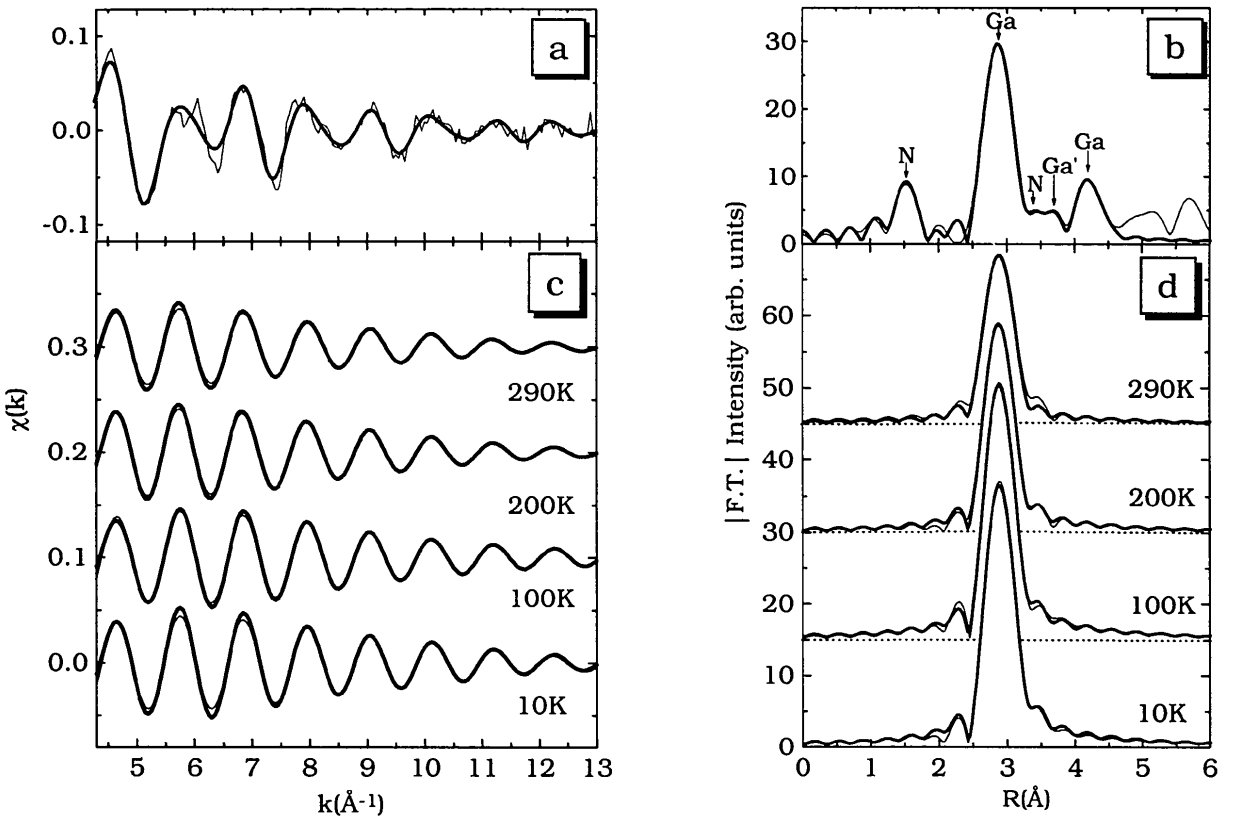

Figure 1

The χ(k) spectra and the corresponding FTs from the hexagonal GaN sample: (a) unfiltered spectrum recorded at T=200K; (b) the corresponding FT (arrows indicate the nn shells); (c) the χ(k) spectra at T=10K, 100K, 200K and 290K, filtered in the R-range 2.2-3.6Å; (d) the corresponding FTs. The experimental curve and the fitting are shown in thin and thick solid lines, respectively.

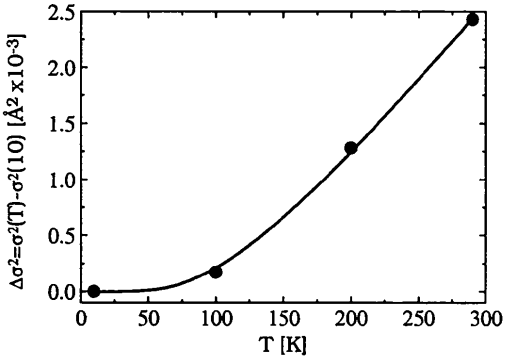

Figure 2

Fitting of $\Delta\sigma^2=\sigma^2(T)-\sigma^2(10K)$ for the Debye–Waller factors of the 2nd nn shell consisting of Ga atoms.

Table 1

Fitting parameters for the 5 nn shells of Ga: type of the nearest neighbors (T_i), nn distances (R_i), coordination numbers (N_i) and Debye-Waller factors (σ^2_i). The shell consisting of the displaced Ga atoms is denoted as Ga′. The coordination numbers expected from the hexagonal model are shown in parenthesis.

T_i	N_i	R_i(Å)	σ^2_i(Å^2) (×10^{-3})
N	4.0±10% (4)	1.94±0.01	4.4±0.2
Ga	10.1±10% (12)	3.18±0.02	3.8±0.4
N	12.0±15% (12)	3.74±0.03	6.7±0.4
Ga′	1.9±20% (0)	3.99±0.05	4.1±0.4
Ga	8.5±25% (6)	4.51±0.04	4.8±0.5

However it should be pointed out that, due to the similarity of the hexagonal and cubic polytypes (Edgar, 1994), the polarization effects in the EXAFS spectra are not significant. The values in the parentheses are the expected, from the model, coordination numbers. As shown in Table 1, the Ga atom is tetrahedrally coordinated. However, the coordination in the 2nd nn shell is distorted. Instead of 12 Ga atoms at a distance R=3.18Å we detect 10 Ga atoms at the expected distance and 2 at a distance longer by 0.8±0.05Å. This distortion is similar to that detected by EXAFS measurements at the nitrogen *K*-edge and is attributed

to nitrogen vacancies. As expected, the results for the cubic sample are, within the error bar, identical to those from the hexagonal sample.

From the temperature dependence of the EXAFS analysis results (measurements at 10K, 100K, 200K and 290K) the Einstein temperature ($\Theta_E=\hbar\omega_E/2\pi k_B$) can be determined. The calculation of Θ_o is based on the values of the DW factor for the 2^{nd} nn shell and the assumption that the Ga-Ga bonds can be treated as Einstein oscillators (Boyce *et al.*, 1989 & Sevillano *et al.*, 1979). For an accurate determination of the DW factor, the χ(k) spectra were Fourier filtered in the R-range 2.15-3.6Å and fitted using a Ga and a N path (2^{nd} and 3^{rd} nn shells). During the fitting, the nn-distances and the coordination numbers for the N and Ga shells were kept fixed at the values listed at Table 1. The Fourier filtered χ (k) spectra, recorded at different temperatures, and the corresponding FTs are shown in Fig. 1(c) and (d), respectively.

The Debye-Waller factor, σ^2, is a sum of two contributions, the σ^2_{stat} and σ^2_{vib} which account for the static and thermal disorder, respectively. Assuming that σ^2_{stat} is temperature independent, the static disorder is elliminated in the difference $\Delta\sigma^2=\sigma^2(T)-\sigma^2(10K)$. The temperature dependence of $\Delta\sigma^2$ for the 2^{nd} nn shell (Ga) is shown in Fig. 2. The σ^2_{vib} is given from the following equation (1) (Boyce *et al.*, 1989):

$$\sigma^2_{vib} = \frac{\hbar^2}{2\Theta_E k_B \mu}\cdot\coth\left(\frac{\Theta_E}{2T}\right) \qquad (1)$$

where μ is the reduced mass of the Ga-Ga atom pair ($\mu = m_{Ga}/2$). The $\Delta\sigma^2$(T) data points in Fig. 2 were fitted using equation (2):

$$\Delta\sigma^2(T) = \frac{A}{\Theta_E}\cdot\left\{\coth\left(\frac{\Theta_E}{2T}\right)-\coth\left(\frac{\Theta_E}{20}\right)\right\} \qquad (2)$$

where A is a constant. The values of A and Θ_E are found equal to 0.77±0.16 and 318±25K, respectively. Given that the Debye temperature of GaN is 600K (Katsikini, 1997), the relationship between Θ_E^{GaN} and Θ_D is : $\Theta_E^{GaN}(\sigma^2)=0.53\Theta_D$.

4. Conclusions

In conclusion, Ga *K*-edge EXAFS measurements on cubic and hexagonal GaN reveal that the microstructure around the Ga atom is distorted. The second nearest neighbor shell, which consists of Ga atoms, is splited and ten Ga atoms are found at the expected distance of 1.94Å while two atoms are found at a distance longer by 0.8±0.05Å. From the temperature dependence of the EXAFS spectra, the Einstein temperature for the Ga-Ga atom pair is found equal to 318±25K.

We would like to thank L. Tröger, M. Tischer and K. Attenkoffer for their support during the experiment at HASYLAB.

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(Received 10 August 1998; accepted 26 January 1999)