Temperature dependent EXAFS of InN

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Received 18 November 2007, accepted 23 November 2007

Published online 25 September 2008

PACS 61.05.cj, 61.66.Fn, 65.40.De, 81.05.Ea

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The effect of temperature on the bonding environment of indium in an InN epilayer is studied using X-ray absorption fine structure (EXAFS) spectroscopy. Shell-by-shell fitting of the EXAFS spectra reveals that, in the temperature range 80–245 K, the change in the nearest neighbour distances is smaller than the uncertainty of the measurement. The Debye–Waller factor of the second neighbouring shell (In–In pair) shows strong temperature dependence. Fitting using the Einstein model yields an Einstein temperature equal to 193 K

± 5%. An alternative way of extracting information on the vibrational properties of the lattice is the simulation using the equation of motion method for the determination of the Debye–Waller factors. The used values of 120 N/m and 50 N/m of the force constants for In–N and In–In bond stretching, respectively, simulate satisfactory the spectra measured at five different temperatures in the range 80–245 K.

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1 Introduction InN is a direct band gap semiconductor which finds applications in optoelectronics for the fabrication of IR light emitting devices and solar cells as well as in microelectronics for the fabrication of high electron mobility transistors. The optical and electronic properties of semiconductors are determined from the band structure which is strongly affected by the presence of stress [1]. In device applications, InN is often subjected to stress since it is found as a component of ternary or quaternary nitride alloys or as a very thin layer in heterostructures. In order to model the behaviour of films under hydrostatic or biaxial stress it is important to know the elastic constants C_{ij} whose values are strongly affected by the force constants α and β for bond stretching and bond bending, respectively [2].

The main kinds of stress in epitaxially grown films are the biaxial thermal stress, due to the different thermal expansion coefficients of the epilayer and the substrate, and hydrostatic stress due to the presence point defects and/or impurities. InN, which is often grown on Al_2O_3 substrates using a GaN buffer layer, can be simultaneously subjected to both biaxial and hydrostatic stress. Temperature de-

pendent X-ray diffraction (XRD) measurements on InN powder provided the following values for its thermal expansion coefficients: $3.6 \times 10^{-6} \text{ K}^{-1}$ and $2.6 \times 10^{-6} \text{ K}^{-1}$ normal and parallel to the c axis, respectively [3]. Temperature dependent XRD measurements on a $10 \text{ }\mu\text{m}$ InN/ $4 \text{ }\mu\text{m}$ GaN/ $300 \text{ }\mu\text{m}$ Al_2O_3 trilayer revealed that the lattice constants of the three layers depend linearly on temperature. The thermal expansion coefficient of InN is found equal to $6.0 \times 10^{-6} \text{ K}^{-1}$ [4]. Finally, according to theoretical calculations the thermal expansion coefficients of bulk InN samples depend on temperature for temperatures lower than 400 K [5].

Here we apply extended X-ray absorption fine structure (EXAFS) spectroscopy in order to study the temperature dependence of the In bonding environment in InN thin films. The EXAFS spectrum maps the dependence of the X-ray absorption coefficient on the energy of the impinging photon, at energies above an edge that corresponds to a core level. The EXAFS oscillations appear due to interference phenomena between the outgoing photoelectron wave and that backscattered from the neighboring atoms.

2 Growth conditions and experimental details

The studied InN film was grown by nitrogen radio frequency molecular beam epitaxy on an Al₂O₃(0001) substrate using a 2-μm-thick GaN buffer layer. The thickness of the InN epilayer, which is grown at 335 °C, was 1.2 μm. Under those growth conditions the resulted InN film was continuous (2D growth mode). The lattice constants were determined by high resolution XRD and they are found equal to: $a = 3.5252 \text{ Å}$ and $c = 5.7078 \text{ Å}$. The good quality of the film is verified by the small width of the (0004) and (10 $\bar{1}$ 5) XRD rocking curves [6].

The In *K* edge EXAFS measurements were conducted at the Synchrotron Radiation Facility HASYLAB in Hamburg at the C beamline. The spectra were recorded in the fluorescence yield mode using a 7-pixel Si(Li) fluorescence detector cooled at 77 K and positioned on the horizontal plane, at right angle to the beam. A liquid He cryostat was used for measurements in the temperature range 80–245 K. In order to avoid polarization effects the angle of incidence to the sample surface was 55°. The spectra were normalized with the incoming photon flux using the signal of an ionization chamber positioned in front of the sample. The analysis of the EXAFS spectra was done using the FEFF8 and FEFFIT programs [7].

3 Analysis Prior to analysis the EXAFS spectra are subjected to subtraction of the atomic background and transformation from the energy space to the *k* (photoelectron wavenumber) space. The resulting $\chi(k)$ spectrum is described by the equation:

$$\chi(k) = \sum_j \frac{1}{kr_j^2} N_j S_i F_j(k) e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j(k)} \sin(2kr_j + \phi_{ij}(k)) \quad (1)$$

i.e. it is a sum of spherical waves with *k*-dependent amplitude. The subscripts *i* and *j* stand for the absorbing atom and its neighbours, respectively. r_j and N_j are the distance and coordination number of the j^{th} nearest neighbour (nn) shell, S_i is the amplitude reduction factor, $F_j(k)$ and $\phi_{ij}(k)$ are the backscattering amplitude and phase, λ_j is the mean free path of the photoelectron and σ_j^2 is the Debye–Waller factor (DWF). The EXAFS DWF is the mean square relative displacement of the absorbing and the neighbouring atoms projected along the bond direction. More specifically, it is defined as:

$$\sigma_j^2 = \langle [\vec{r}_j \cdot (\vec{u}_j - \vec{u}_i)]^2 \rangle \quad (2)$$

where $\vec{u}_j$ and $\vec{u}_i$ are the displacements of the neighbouring and absorbing atom, respectively.

Structural information from the EXAFS spectra is usually obtained by fitting the $\chi(k)$ spectrum with a sum of photoelectron scattering paths using a proper starting model which provides the initial fitting values. The photoelectron scattering path can be either a single scattering

path, which corresponds to the direct scattering to the neighbouring shell, or a multiple scattering path which includes scattering by more than one neighbours.

The $\chi(k)$ spectrum can be also simulated using a cluster of atoms around the absorbing atom. The necessary DWFs can be calculated using the equation-of-motion (EM) method. The force constants α and β for bond stretching and bond bending can be used as an additional input and they can be varied until the simulation and the experimental curve coincide [8].

Figure 1 Fourier transform of the k^2 weighted $\chi(k)$ spectra of the InN sample recorded at various temperatures. The experimental curve and the fitting are shown in thin and thick solid lines, respectively.

Table 1 Results of the shell-by-shell fitting of the spectra recorded at various temperatures. *R* is the nn distance and σ^2 is the DWF. The listed errors are the uncertainties provided by the fitting program.

		Measurement temperature				
		80 K	120 K	150 K	200 K	250 K
In-N	$R_1(\pm 0.01) \text{ Å}$	2.16	2.15	2.15	2.15	2.15
	$\sigma_1^2(\pm 0.6) \text{ Å}^2 \times 10^{-3}$	1.7	4.2	3.4	3.5	3.4
In-In	$R_2(\pm 0.005) \text{ Å}$	3.528	3.533	3.531	3.531	3.533
	$\sigma_2^2(\pm 0.2) \text{ Å}^2 \times 10^{-3}$	2.5	3.4	3.9	5.0	5.8
In-N'	$R_3(\pm 0.02) \text{ Å}$	4.16	4.13	4.17	4.17	4.16
	$\sigma_3^2(\pm 1) \text{ Å}^2 \times 10^{-3}$	6	5	3	4	7

4 Results and discussion

4.1 Shell-by-shell fitting The EXAFS analysis proceeds with the shell-by-shell fitting using the photoelectron scattering paths which contain the theoretically calculated backscattering amplitude and phase as well as the mean free path of the photoelectron.

The $\chi(k)$ spectra of the InN sample recorded at 80, 120, 150, 200 and 245 K were fitted simultaneously up to the third nn shell, using both the k^2 and k^3 weighting schemes. The coordination numbers were kept fixed to the values predicted by the model of the wurtzite InN, i.e. 4 N atoms in the first, 12 In atoms in the second and 9 N atoms in the third nn shell. The amplitude reduction factor and the shift of the energy origin were simultaneously iterated in all the spectra and their values were found equal to 1.02 ± 0.03 and 1.9 ± 0.3 eV, respectively. The fitted spectra plotted in the R-space are shown in Fig. 1 and the fitting results are listed in Table 1.

Our results demonstrate that the nn distances are not temperature dependent. The thermal strain in the growth plane, $\varepsilon_{||}$, is calculated using the equation:

$$\varepsilon_{||} = \Delta T \cdot \Delta \alpha \quad (3)$$

where $\Delta \alpha$ is the difference of the thermal expansion coefficients of InN and Al_2O_3 [3] and ΔT is the difference between the measuring and growth temperatures. The variation of the a lattice constant in the temperature range 80 K to 245 K is 0.065% which is smaller than the error in the EXAFS analysis.

On the contrary, the DWF factors of the second nn shell, that consists of In atoms, are found to increase with temperature (Fig. 2). In order to extract information on the vibrational properties of the In sublattice the spectra were fitted using the Einstein model which assumes that the atoms in the In sublattice oscillate like simple harmonic oscillators of frequency ω_E . The relation between the Einstein frequency and the Einstein temperature, Θ_E , is given by:

$$\Theta_E = \frac{\hbar \omega_E}{k_B} \quad (4)$$

where k_B and $\hbar$ are the Boltzmann and Planck constants. According to the Einstein model, the dependence of the DWF on the temperature is described by the equation:

$$\sigma^2 = \frac{\hbar^2}{2\Theta_E k_B \mu} \coth\left(\frac{\Theta_E}{k_B T}\right) \quad (5)$$

where μ is the reduced mass of the In–In pair. The $\frac{\hbar^2}{2k_B \mu}$ factor for the In sublattice is equal to $0.419 \text{ \AA}^2\text{K}$. Fitting using the Einstein model resulted to a value of Θ_E equal to $193\text{K} \pm 5\%$ [9, 10]. This value of Θ_E corresponds to the Einstein frequency $\omega_E = 2.53 \times 10^{13} \text{ s}^{-1}$ or equivalently

$134 \text{ cm}^{-1} \pm 5\%$. This value of ω_E belongs in the lower region of phonon density of states (DOS), which extends from 0 to 230 cm^{-1} and includes the acoustic modes and the B_1 and E_2 optical modes [11]. This region is dominated by the In atom vibrations contrary to the high frequency part of DOS that is dominated by the motions of the much lighter nitrogen atoms.

Figure 2 Temperature dependence of the Debye–Waller factor (dots) of the In–In shell. The thick line corresponds to the dependence predicted by the Einstein model using for the Einstein temperature the value of 193 K. The dashed lines show the effect of the variation of the Einstein temperature by $\pm 5\%$ on the fitting curve.

4.2 Simulation using the equation of motion method Additional information on the strength of the interaction between the In and N atoms is obtained using the EM method for the calculation the DWF. The $\chi(k)$ spectra recorded at the temperatures of 80 K, 120 K, 150 K, 200 K and 245 K were simulated using a cluster of radius equal to $6.2 \text{ \AA}$ around the absorbing atom. The cluster was generated using a unit cell with $P6_3mc$ symmetry and the XRD determined values of the a and c lattice constants. The internal u parameter was set equal to 0.375. The atomic scattering potentials were calculated self consistently in a cluster of $5 \text{ \AA}$ radius [7]. The best simulation for the spectra recorded at the five different temperatures was obtained for bond stretching force constants for the In–N ($\alpha_{\text{In–N}}$) and In–In ($\alpha_{\text{In–In}}$) pairs equal to 120 N/m and 50 N/m, respectively. The simulation spectrum is plotted along with the experimental spectrum in the k- and R-space in Figs. 3 and 4, respectively.

5 Conclusion Temperature dependent EXAFS, in the range 80–245 K, was applied for the study of InN epitaxially grown on Al_2O_3 . It is found that the variations of the nearest neighbour distances are smaller than the detection limit of the EXAFS technique. The DWF of the In–In pair depends strongly on the temperature. Application of the

Einstein model to fit the DWF versus temperature dependence yields an Einstein temperature equal to $193 \text{ K} \pm 5\%$ for the In sublattice.

Figure 3 Simulation of the EXAFS spectra in the k -space using the EM method for the calculation of the DWF. The experimental and the simulation curves are shown in thin and thick lines, respectively.

Figure 4 Simulation of the EXAFS spectra in the R -space using the EM method for the calculation of the DWF. The experimental and the simulation curves are shown in thin and thick lines, respectively.

Simulation of the EXAFS spectra with the equation of motion method for the calculation of the DWF and using a cluster with radius equal to 6.2 Å around the absorbing atom is quite satisfactory over a wide temperature range. The values for the In–N and In–In pair bond stretching force constants are found equal to 120 N/m and 50 N/m , respectively.

Acknowledgements This work was supported by the EC under the contract MRTN-CT-2004-005583 (PARSEM). The measurements at HASYLAB were financially supported by the EC IA-SFS program under the contract RII3-CT-2004-506008.

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