ANGULAR DEPENDENCE OF THE NEXAFS STRUCTURE IN HEXAGONAL AND CUBIC GaN.

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ABSTRACT

Cubic and hexagonal GaN thin films, grown epitaxially on Si and Al_2O_3, respectively, are studied using the angular dependence of the near edge X-ray absorption fine structure (NEXAFS) spectra recorded at the N-K-edge. It is shown that the intensities of the individual resonances are independent of the angle of incidence θ if the material is pure β-GaN (zinc-blende), while they have a linear dependence on $\cos^2\theta$ if the material has hexagonal symmetry (α-GaN). Furthermore, it is demonstrated that deviations from the α- or β-phases (mixed-phase samples) are clearly detectable since they lead to a systematic energy shift in the NEXAFS resonances, the extent of which depends on the percentage of the α- or β-allotropic structures. Based on these observations it is proposed that the NEXAFS spectra can be used as a fingerprint of the symmetry of the examined crystal.

I. Introduction.

GaN has been a subject of intensive study because it finds applications in visible-UV light emitters and detectors as well as high-frequency, -temperature and power devices[1]. It can be grown either as hexagonal (wurtzite) α-GaN or as cubic (zinc blende) β-GaN. However, the stabilization of the β-GaN polymorph is difficult and growth of crystals that contain both α- and β-GaN is often observed[2]. Near edge X-ray absorption fine structure (NEXAFS) spectroscopy, which has been extensively used to determine the symmetry of adsorbed molecules on surfaces[3], could also find application in crystalline materials where the energy position and the intensity of the NEXAFS resonances depends on the group symmetry. In this work we propose the application of NEXAFS for the identification of deviations from the cubic or hexagonal symmetries in epitaxially grown GaN films.

II. Sample preparation and experimental details.

The samples were grown at 600°C on Si and Al_2O_3 substrates by microwave plasma electron cyclotron resonance-assisted molecular beam epitaxy (ECR-MBE). The α-GaN (GaN179) was grown on (0001) plane of Al_2O_3 (film thickness d=1.67μm),

the β-GaN (GaN57) was grown on p-Si (100) (d=1,60μm) while a mixed phase sample (GaN67) was grown on n-Si (111) (d=0,80μm). Details on the growth conditions[4,5] and structural information from transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements[6,7] has been reported previously.

The NEXAFS spectra were recorded at room temperature, at the N-K-edge (390-440eV), using the SX-700-I plane grating monochromator at the electron storage ring BESSY in Berlin. Detection was in the fluorescence mode using a high purity Ge detector, and the NEXAFS spectra were recorded as a function of the angle of incidence θ which is defined by the incident beam and the sample surface (as shown in the inset of Fig.1).

III. Results and discussion.

The NEXAFS spectra were fitted using a step-function to simulate the absorption edge and a number of gaussians to fit the individual resonances. Prior to fitting the spectra were subjected to linear background subtraction and normalized to the atomic limit. A typical fitting of the NEXAFS spectrum recorded for θ=80° from the hexagonal sample GaN179 is shown in Fig. 1.

For cubic symmetry, the allowed transitions are $1a_1 \rightarrow t^*_2$, where t_2 belongs to a 3-dimensional irreducible representation (T_2) of the group T_d and is observed with the same intensity for all angles of incidence. The allowed transitions for the C_{6v} hexagonal symmetry are $1a_1 \rightarrow a_1^*$ and $1a_1 \rightarrow e^*_1$ which are strongest for grazing and normal incidence, respectively[8]. In the $1a_1 \rightarrow a_1^*$ transition the final state can result from mixing of s and p_z orbitals while in $1a_1 \rightarrow e^*_1$ the final state can result from mixing of p_x and p_y orbitals.

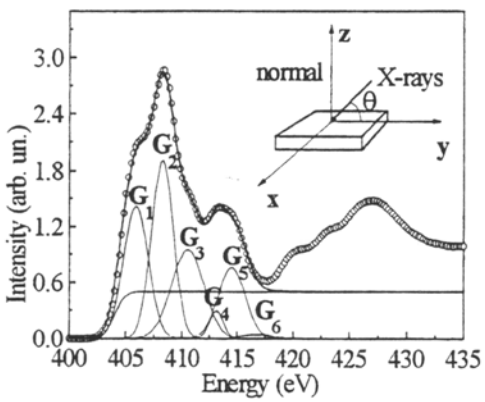

Fig. 1 : Fitting of the NEXAFS spectrum from the hexagonal sample GaN197 for θ=80°.

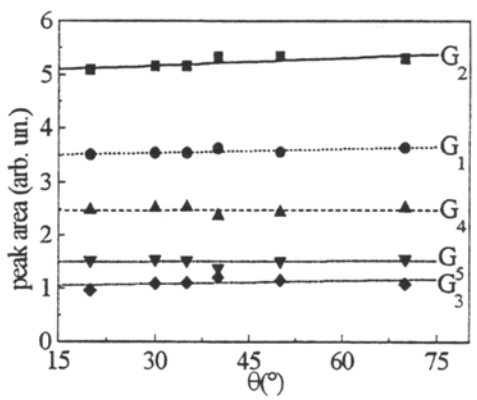

Fig 2 : Area of the resonances in the NEXAFS spectra of the cubic sample GaN57 as a function of the angle θ.

The energy position ΔE_i of the individual NEXAFS resonances is measured relative to the absorption edge, which is defined as the inflection point of the step

function. The area under the resonances as a function of θ from the samples β-GaN57 and α-GaN179, are shown in Fig. 2 and 3, respectively. As shown in Fig.2 the areas under the resonances in the spectra from GaN57 are, within the experimental error, independent of θ. This result is in agreement with the expected behavior of a cubic sample. According to previously reported XTEM and XRD results the GaN57 is pure cubic with less than 1% of co-existing hexagonal polytype[6,7]. Contrary to that, the NEXAFS spectra from the hexagonal sample have a strong angular dependence as shown in Fig.3. In this figure, the areas under the peaks are normalized to the area corresponding to the "magic" angle, i.e. the characteristic angle for a sample with C_{6v} hexagonal symmetry for which the NEXAFS spectra are independent of the angle between the final state vector or plane molecular orbital and the normal to the sample surface. The magic angle for the hexagonal sample GaN179 with C_{6v} hexagonal symmetry was found to be equal to θ=54.7°.

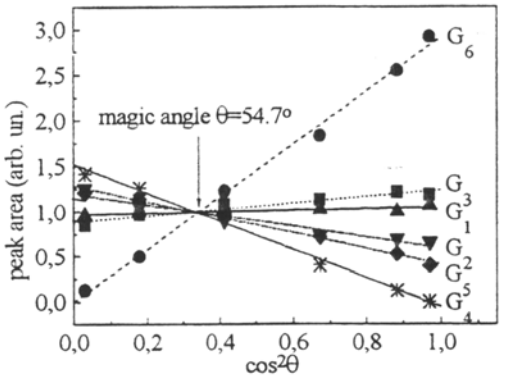

Fig.3 : Areas under the NEXAFS resonances as a function of $\cos^2\theta$ for the hexagonal sample GaN179.

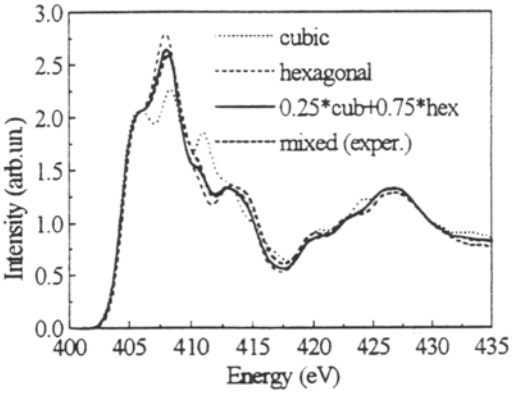

Fig. 4 : NEXAFS spectra from the mixed, the cubic and the hexagonal samples and the calculated spectrum assuming 25% cubic and 75% hexagonal contributions, respectively.

The characteristics ΔE_i, full width at half maximum (FWHM) and amplitude of the gaussians used for the fitting of the NEXAFS resonances from the mixed sample are found to depend on the angle of incidence and they are different from those corresponding to the α- and β- GaN. It should be pointed out that ΔE_i and the corresponding FWHM are constant for the pure cubic and hexagonal samples, for any θ. The characteristic energies ΔE_i for the α- and β-GaN are listed in Table 1.

Table 1 : Energy positions of the resonances in the NEXAFS spectra for the pure α- and β-GaN samples. The errors due to the fitting are smaller than the 100meV step used for the measurements.

sample	ΔE_1 (eV)	ΔE_2 (eV)	ΔE_3 (eV)	ΔE_4 (eV)	ΔE_5 (eV)	ΔE_6 (eV)
β-GaN57	1,80	4,70	7,20	8,70	11,40	-
α-GaN179	1,90	4,20	6,50	9,10	10,50	12,70

From the values listed in Table 1 it is shown that the energy position of all the resonances, with the exception of G_1 which appears at the same energy for all the examined crystals (because it corresponds to orbitals directed along the magic angle), depends on the crystal symmetry. If the sample is mixed, then the energy position of the resonances shifts with θ between the limits set by the cubic and hexagonal structures. Given the constancy of the ΔE_i for pure cubic and hexagonal phases, it can be proposed that the NEXAFS spectra can be used as a fingerprint of the α- or β-GaN phases, while any deviation of the ΔE_i's indicates the coexistence of both α- and β-GaN, i.e. a mixed-phase sample.

The NEXAFS spectra from a mixed-phase sample can be approximated by the weighted average of the spectra from the pure cubic and hexagonal samples, where the weight factors reflect the fraction of the cubic and hexagonal phases in the sample. Following this procedure the NEXAFS spectrum from the mixed-phase sample GaN67 can be reproduced by averaging the NEXAFS spectra from the pure cubic and hexagonal samples weighted by 25% and 75%, respectively. The resulting spectrum is shown in Fig.4 (continuous line) along with the recorded spectra from the mixed (thick dashed line), the cubic (dotted line) and hexagonal (dashed line) samples. As shown in the figure, this simple model for the NEXAFS structure of the mixed crystal predicts the experimental spectrum quite accurately.

IV. Conclusions

It is demonstrated that the NEXAFS spectra can be used as a fingerprint of the cubic or hexagonal symmetry for GaN. The energy positions of the resonances are independent of the angle of incidence for either polytype, while their oscillators strengths (areas under the Gaussians) are independent of the angle of incidence only if the sample is pure cubic. Mixing of the α- or β-GaN phases can be detected as an angle-dependent shift of the energy positions of the NEXAFS resonances from the values corresponding to a pure cubic or hexagonal sample. Application of the procedure to the mixed-phase sample GaN67 has yielded results that are in very good agreement with those from XRD and high-resolution TEM measurements[6,7].

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