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Nitrogen *K*-edge NEXAFS measurements on group-III binary and ternary nitrides

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It is demonstrated that the NEXAFS spectra are a “fingerprint” of the microstructure and the composition of the AlGa_{1-x}N and InGa_{1-x}N alloys. From the angular dependence of the NEXAFS spectra, the hexagonal symmetry of the compounds under study is deduced and the (*p_x*, *p_y*) or *p_z* character of the final state is identified. The energy position of the absorption edge (*E_{abs}*) of the binary compounds depends on the cation atomic number. The *E_{abs}* of the AlGa_{1-x}N alloys takes values in between those corresponding to AlN and GaN, as was expected. Contrary to that, the absorption edge of In_{0.16}Ga_{0.84}N is red-shifted relative to that of GaN and InN, probably due to ordering and/or phase separation phenomena.

Keywords: Nitrides; In_xGa_{1-x}N; Al_xGa_{1-x}N; NEXAFS; density of states.

1. Introduction

Alloys of group III nitrides have attracted a lot of interest because they permit band-gap engineering and fabrication of emitters and detectors operating at wavelengths in the range from orange to UV (Nakamura *et al.*, 1997). The binary compounds AlN, GaN and InN exist in the wurtzite (hexagonal, P6₃mc) and the zinc-blende (cubic, F-43m) polytypes. Angular-dependent near edge X-ray absorption fine structure (NEXAFS) and extended X-ray absorption fine structure (EXAFS) measurements at the N and Al *K*-edges of undoped GaN and AlN were recently reported by Katsikini *et al.* (1996, 1997a, 1997b, 1998). It was shown that the NEXAFS spectra are a fingerprint of the crystal symmetry (Katsikini *et al.*, 1998) while the nearest neighbor distances N-Ga are distorted due to presence of native defects (Katsikini *et al.*, 1997b). Here we apply NEXAFS spectroscopy in order to study the dependence of the N_p-partial density of unfilled states in the conduction band (CB) on the cation of the binary and ternary alloys Al_yGa_{1-y}N and In_xGa_{1-x}N. Furthermore,

angular dependent measurements are used to verify the hexagonal nature of the films.

2. Growth conditions and experimental details

The binary AlN, GaN, InN and ternary In_xGa_{1-x}N (*x*=0.16), Al_yGa_{1-y}N (*y*=0.25, 0.5) nitrides were grown by electron cyclotron resonance molecular beam epitaxy on (0001) Al₂O₃ substrates, in the temperature range 700–800°C. All the epilayers were about 1 μm thick with the exception of

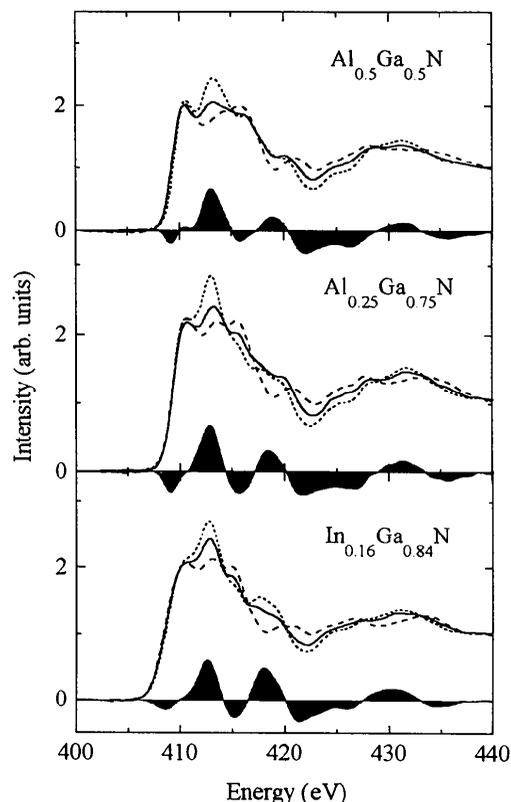


Figure 1

N *K*-edge NEXAFS spectra recorded at three different angles of incidence: normal (dotted line), grazing (dashed line) and at the magic angle (continuous line) of the under study ternary nitrides. The difference spectra (spectrum at grazing incidence subtracted from that at normal incidence) are also shown at the lower part of each figure.

the In-containing compounds, which were 0.3–0.4 μm thick. Details on the growth conditions and the structural properties of the films have been reported previously (Moustakas *et al.*, 1993, Korakakis & Moustakas, 1997, Singh *et al.*, 1997).

The NEXAFS spectra were recorded at room temperature, at the N *K*-edge (400–450 eV) using the SX-700-I monochromator at the electron storage ring BESSY-I in Berlin. The energy resolution of the monochromator at 400 eV, for the used slit of 100 μm, is 0.8 eV. Detection was in the fluorescence (FLY) yield mode using a high purity Ge

detector. The NEXAFS spectra were recorded at three different angles of incidence (ϑ , measured from the sample surface): near-normal incidence (ϑ_{\parallel}), grazing incidence (ϑ_{\perp}) and at the “magic angle” (ϑ_{ma}). For hexagonal samples, with the c axis normal to the sample surface, $\vartheta_{ma}=54.7^{\circ}$ (Stöhr, 1992, Katsikini *et al.*, 1998). Details of the experimental geometry and the measurement conditions have been reported previously (Katsikini *et al.*, 1996, 1998).

3. Results and discussion

The energy positions of the absorption edge (E_{abs}) and the NEXAFS resonances (E_i) were determined from fitting of the spectra in the energy range 400–422eV using a sigmoidal (Boltzmann function), to simulate transitions to the continuum, and six gaussians (G_i , $i=1\dots6$), to simulate transitions to bound states. The E_{abs} is defined as the inflection point of the sigmoidal. Prior to fitting the spectra were normalized to the primary beam current and they were subjected to linear background subtraction (by fitting the pre-edge region) and normalization to the atomic limit (~ 440 eV).

The allowed transitions in hexagonal materials are from the initial $N1s$ state of a_1 symmetry to final Np states, i.e. $1a_1 \rightarrow a_1^*$ and $1a_1 \rightarrow e_1^*$ (Cotton, 1971, Stöhr, 1992). The a_1^* states result from mixing of s and p_z atomic orbitals (vector-like orbitals) and should be strongest for grazing incidence, while e_1^* states result from mixing of p_x and p_y atomic orbitals (plane orbitals) and should be strongest for normal incidence. As it was recently reported (Katsikini *et al.*, 1997, 1998), in pure hexagonal AlN and GaN the energy positions and the full width at half maximum (FWHM) of the various gaussians which simulate the NEXAFS transitions do not depend on the angle of incidence, while the area under the gaussians depends linearly on $\cos^2\vartheta$.

The N K -edge NEXAFS spectra of the under study ternary alloys for three values of ϑ are shown in Fig. 1. The difference spectra (spectrum recorded at ϑ_{\parallel} subtracted from that recorded at ϑ_{\perp}), which permit a more accurate determination of the energy positions E_i of the resonances, are also shown at the bottom of each figure. The characteristics of the absorption edge (E_{abs} and width of the step function W_{abs}) and the E_i are listed in Table 1. Among the six gaussians, the G_1 , G_3 and G_6 have maximum intensity at grazing incidence (negative peaks in the difference spectra) and thus they correspond to transitions to p_z final states (vector-like antibonding electron charge distribution). The gaussians G_2 , G_4 and G_5 have maximum intensity at normal incidence and thus they correspond to transitions to (p_x, p_y) final states (plane-like antibonding electron charge distribution). From the analysis it was found that the energy positions and the FWHM of the gaussians for each sample are independent of ϑ . Therefore the criterion developed previously for GaN and AlN (Katsikini *et al.*, 1996, 1997a, 1998) applies to InN and the ternary alloys and thus it can be concluded that these samples have hexagonal symmetry too.

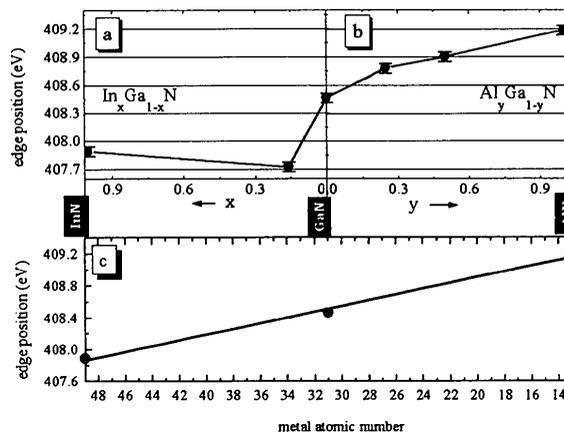


Figure 2

The variation of the energy position of the absorption edge (and the CB minimum) as a function of the (a) In fraction in the $In_xGa_{1-x}N$ alloys, (b) Al fraction in the $Al_yGa_{1-y}N$ alloys and (c) cation atomic number in the binary compounds AlN, GaN and InN.

As shown in Table 1, the absorption edge shifts to lower energy with increasing atomic number Z_C of the cation while the width of the absorption edge W_{abs} (measured from the width of the sigmoidal) increases. This is clearly seen in Fig.2 (a) for InN, $In_{0.16}Ga_{0.84}N$ and GaN and 2(b) for GaN, AlN, $Al_{0.25}Ga_{0.75}N$ ($y=0.25, 0.5$). In Fig. 2(c) the dependence of the position of the absorption edge on the cation/metal atomic number is shown for the binary compounds. More specifically, the W_{abs} (which is a measure of the effective mass m_e^*) increases from AlN to GaN and to InN (i.e. with increasing Z_C), in accordance with the reported values of m_e^* : $m_e^{*AlN}=0.3m_0$ (Miwa & Fukumoto, 1993), $m_e^{*GaN}=0.3m_0$ (Elhamri *et al.*, 1998) and $m_e^{*InN}=0.3m_0$ (Yeo *et al.*, 1998). The variation of W_{abs} with m_e^* can be fitted using the equation: $W_{abs}=0.8-2 \cdot m_e^*$

Table 1

Absorption edge (E_{abs}) and width (W_{abs}) of the sigmoidal and energy positions of the gaussians (E_i) used to simulate the NEXAFS resonances.

		sample name					
parameters		AlN	$Al_{0.5}Ga_{0.5}N$	$Al_{0.25}Ga_{0.75}N$	GaN	$In_{0.16}Ga_{0.84}N$	InN
E_{abs} (eV)		409.2	408.9	408.8	408.5	407.7	407.9
W_{abs} (eV)		0.20	0.25	0.35	0.40	0.50	0.60
E_i (eV)	G_1	410.6	410.4	410.5	410.7	410.1	410.6
	G_2	413.2	413.0	413.1	413.2	412.7	413.2
	G_3	415.0	415.3	415.6	415.5	415.3	415.7
	G_4	416.8	416.9	417.8	417.7	417.6	417.6
	G_5	418.6	419.1	419.9	419.5	419.2	419.2
	G_6	421.2	421.2	421.7	421.5	421.1	421.3

The E_{abs} of InN is shifted by 0.6eV to lower energies relative to that of GaN (Fig. 2(a)) while that of GaN is 0.7eV shifted to lower energies relative to that of AlN (Fig. 2(c)). The E_{abs} of the $Al_yGa_{1-y}N$ alloys appears, as expected, at

energies between the E_{abs} of GaN and AlN. Contrary to that the E_{abs} of $\text{In}_{0.16}\text{Ga}_{0.84}\text{N}$ (and the whole spectrum) is red shifted relative to that of GaN and InN. Such an "anomaly" in the E_{abs} could be attributed to ordering effects and/or phase separation phenomena (Doppalapudi *et al.*, 1998) which have been reported for InGaN.

4. Conclusions

In conclusion, the Np absorption threshold of the group III binary and ternary nitrides is found to shift towards lower energies with increasing atomic number of the cation (Z_C). In the $\text{Al}_y\text{Ga}_{1-y}\text{N}$ alloys the Np absorption threshold appears between that of GaN and AlN and shifts towards higher energies with y while an unexpected red shift is found in the InGaN alloy relative to the absorption edge of GaN and InN. The red shift could be attributed to ordering or phase separation phenomena. The energy positions and widths of the NEXAFS resonances are independent of ϑ while their intensity follows the pattern expected for $1a_1 \rightarrow a_1^*$ and $1a_1 \rightarrow e_1^+$ transitions. Therefore, it can be concluded that the ternary compounds have hexagonal symmetry as their parent binary compounds.

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