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X-ray absorption spectroscopy in the analysis of GaN thin films

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Stoichiometric amorphous GaN thin films have been grown by an ion-assisted deposition method and examined by x-ray photoelectron spectroscopy and x-ray absorption near-edge spectroscopy (XANES). The crucial question is the nature of the local structure around the N and Ga in the x-ray amorphous films. The N K edge XANES has been used to determine coordination around the N centre and reveals substantial differences to crystalline GaN. Although the transitions observed mirror those of the crystalline material and are consistent with density of states calculations, the low-energy peak at ∼402 eV is dominant in all films less than ∼150 nm in thickness. This peak, initially attributed to an sp^2 environment, is associated with the presence of molecular nitrogen. For thicker films, a duplex-type structure is observed with a surface layer much closer to the structure of the crystalline material. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: GaN; ion-assisted deposition; XANES; XPS

INTRODUCTION

Gallium nitride is a wide-bandgap semiconductor material of great interest owing to its use in blue light-emitting devices and other optoelectronic applications.[1] Commercial use is generally based on device structures utilizing epitaxial growth of GaN on sapphire substrates. This arrangement is far from ideal in terms of the lattice match of the two materials but appears to perform satisfactorily in devices despite the relatively high defect density, particularly around the interface with the substrate. The lattice matching issue has prompted a number of investigations of the properties of amorphous GaN thin films,[2–4] in the hope that these substrate-independent materials might have useful optoelectronic properties.

Amorphous GaN films have been prepared successfully in our studies using an ion-assisted deposition (IAD) method,[5] which is a convenient method of depositing dense and homogeneous films with excellent control of stoichiometry. The method is described in detail elsewhere but the essential feature is the co-deposition of material and energy from the ion beam, which provides a convenient route to overcome energy barriers to reaction. In this case, the evaporation of Ga is carried out in the presence of an energetic nitrogen ion beam from a Kaufman-type source (Fig. 1). The films reported in this work were deposited with the use of a 500 eV beam and range in thickness from 40 to 400 nm. These films have been deposited on a variety of substrates, including silicon wafers, quartz, glassy carbon and mylar, and their optoelectronic properties examined.[6]

Rutherford backscattering spectroscopy data confirm the 1 : 1 stoichiometry of the films[5] but the crucial questions that arise in the characterization of these films revolve around whether they are truly amorphous. Debye-Scherrer analysis of the (1122) peak of the GaN x-ray diffraction pattern suggests a crystallite size of <10 nm but there is some evidence from transmission electron microscopy (TEM) and electron diffraction suggesting a degree of short-range order in the films.[7] Thus, the local geometry around the nitrogen and gallium is of particular interest.

X-ray photoelectron spectroscopy (XPS) is an analytical method unique in the combination of elemental identification, quantitation and sensitivity to chemical state that it offers. However, XPS is essentially a core-level spectroscopy and chemical-state sensitivity is based on the indirect effect on the shielding and deshielding of core levels due to changes in the electron density and distribution of the electrons involved in bonding, i.e. those occupying the valence band. The binding energy (BE) of a core level is thus measurably shifted by factors that affect this electron distribution. Most sensitive are changes in formal oxidation state, whereas geometrical effects such as differing coordination geometries are more difficult to resolve. In favourable cases geometrical effects alone can be resolved, such as the 0.6 eV shift that distinguishes the octahedral and tetrahedral coordination of Al,[8] but this is the exception rather than the rule. In the case

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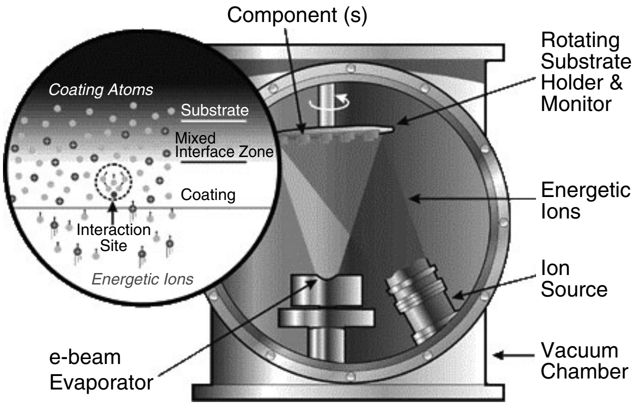

Figure 1. Schematic of the apparatus used for ion-assisted deposition of amorphous GaN thin films.

of these GaN films, it was necessary to find an analytical method that provides more sensitivity than XPS to the local chemical environment.

Such information potentially can be provided by a combination of x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS). Spectra are obtained by scanning the photon energy over the absorption edge and for several hundred above the threshold. The EXAFS region, typically starting at >50 eV above the absorption edge, is commonly used to determine coordination numbers and coordination radii, and the single scattering processes involved are relatively well understood. However the soft XANES region, where photon energies lie within 50 eV of the edge, is substantially richer in information about the chemical environment but is also less well understood.

The XANES technique is especially useful in examining semiconductor materials because bound states at the ionization threshold are probed. In the case of a semiconductor such as GaN, these vacant states lie at the bottom of the conduction band. With a knowledge of the predicted density of states, it is thus possible to determine from the spectrum the microstructural and electronic changes that influence this density of states. Thus x-ray absorption in the N K near-edge region gives excitation to unoccupied bound states (largely p-type, as dictated by symmetry) in the bottom of the conduction band.

The N K edge region, starting at ~400 eV, also provides an excellent example where a sufficient energy window for the EXAFS experiment is not available, because of the relatively low energy and the ubiquitous contribution of residual oxygen to these spectra. However, the proximity to the valence levels means that the chemical detail in the near-edge region is extremely good. This paper thus examines the utility of the XANES spectrum in the microstructural analysis of these materials with reference to that of the conventional XPS spectrum.

EXPERIMENTAL

Samples were prepared by the IAD method discussed in detail elsewhere.[5] The near-stoichiometric films are deposited with a nitrogen flux of around five times the flux of the evaporated Ga, at a beam energy of ~500 eV. A particular area of interest was the effect of film thickness, which is controlled by deposition time and varied between 40 and 400 nm.

The XANES spectra were collected on the spherical grating monochromator (SGM) beamline of the Canadian Synchrotron Radiation Facility (CSRF) located at the Synchrotron Radiation Centre (SRC) of the University of Wisconsin, Madison.[9] The typical photon intensity distribution of this line peaks at ~300 eV, thus the study of the N K edge at ~400 eV is particularly well suited to this line. Spectra were collected at normal incidence in both the total electron yield (TEY) and fluorescence modes, in an energy range from ~10 eV below edge to 30 eV above the edge. Photon flux was recorded for background subtraction and normalization using a 90% transmission grid.

RESULTS AND DISCUSSION

A monochromatized Al-excited XPS spectrum of a crystalline (Al,Ga)N sample is shown in Fig. 2. The difficulties with the XPS characterization of such samples are immediately apparent. For Al excitation, the strong Ga LMM Auger transitions mask the N 1s peak at ~400 eV and the most accessible Ga 3d and 2p transitions lie at the boundaries of the spectral window. Neither transition is optimal in terms of the chemical sensitivity. The Mg-excited spectrum certainly allows examination, with rather less chemical resolution, of the N 1s peak position, but in narrow scans we detect no resolvable peak shifts between the amorphous and crystalline GaN materials. It can be seen that the conventional XPS spectrum is poorly suited to answering the questions surrounding the microstructure and properties of these amorphous GaN films.

The N K edge XANES spectra of a crystalline GaN sample and an amorphous ion-assisted deposited GaN film are shown in Fig. 3, as collected on the SGM line of the CSRF. The spectrum of the crystalline material is consistent with several from the literature.[10,11] A peak envelope is observed corresponding to transitions from the N 1s level to vacant low-lying levels in the conduction band. Lambrecht *et al.* provide a band structure and density of states analysis for wurtzite-type GaN.[10] As anticipated, the experimental

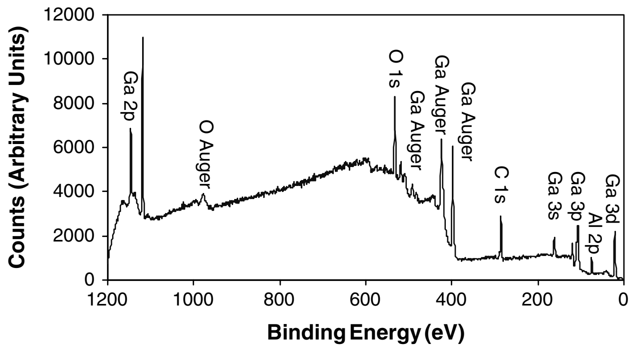

Figure 2. The monochromatized Al-excited XPS spectrum of a crystalline AlGaN sample. The prominent Ga Auger transitions mask the N 1s peak at ~400 eV. The spectrum was provided by Professor John Grant, University of Dayton.

XANES spectrum closely matches this density of states for the lowest lying levels above the bandgap, projected onto the vacant N 2p levels.

The corresponding spectrum from the stoichiometric, x-ray amorphous 250 nm ion-assisted deposited GaN film is also shown in Fig. 3. It is apparent that although broadly the same components in the envelope are observed in the near-edge region, consistent with the assignments of Lambrecht and others,[10,11] the relative contributions of the individual transitions are very different. The crucial difference lies in the transitions centred at 402 and 404.5 eV. The thinner amorphous films show complete dominance of the lower energy peak, whereas thicker films show substantially increased contributions of the 404.5 eV peak, particularly in the more surface-sensitive TEY spectrum. The two peaks are widely attributed to sp^2 and sp^3 dominated environments, respectively,[10,11] assignments supported by Terminello *et al.*[12] in examining boron nitrides of various structures. This approach has been applied to transition metal nitrides to distinguish sp^2 ($1s \rightarrow \pi^*$) and sp^3 ($1s \rightarrow \sigma^*$) environments.[13] Thus it is tempting to suggest that although the bonding environment in the films resembles that of the crystalline materials, disorder in the amorphous films is accompanied by substantially increased distortion or vacancies in the tetrahedral geometry around the nitrogen.

This problem was resolved with scans across the 402 eV peak at a resolution of better than 100 meV, which reveals that this peak corresponds to molecular nitrogen, with the complete vibrational envelope resolved (Fig. 4).[9] Thus it is proposed that the 402 eV peak is associated with the presence of significant amounts of interstitial molecular nitrogen. The dominance of this peak in the thinner films then raises the question as to how this molecular nitrogen is distributed with depth and what causes this distribution. Films 70–400 nm thick reveal significant differences in electron diffraction patterns, with some evidence of a more crystalline structure in the thicker films.[7] This is supported by cross-sectional TEM images, which reveal evidence of a duplex-type structure in the thicker films, with the near-surface layer showing increasing ordering.

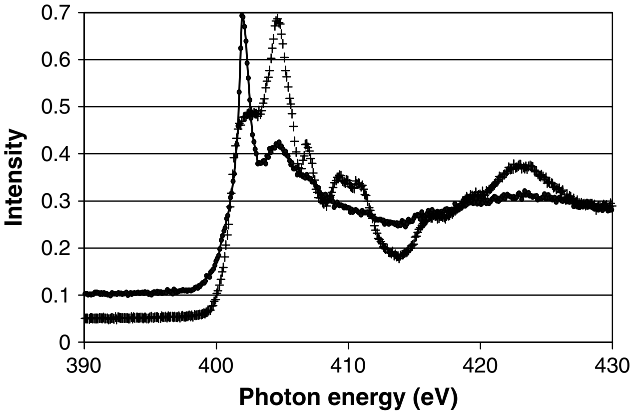

Figure 3. Nitrogen K edge XANES spectra, recorded in fluorescence mode, of crystalline GaN (+) and ion-assisted deposited amorphous GaN film (solid line).

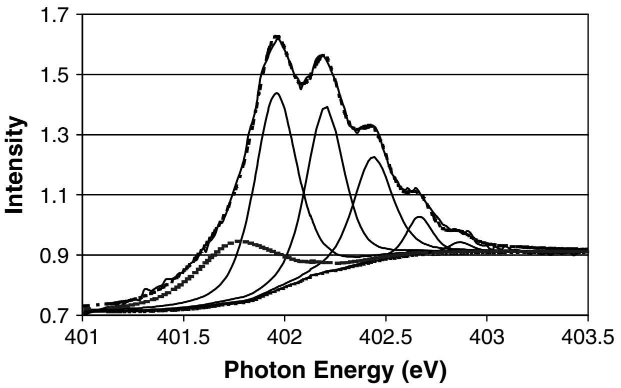

Figure 4. High-resolution (<100 meV) spectrum of the 402 eV peak, revealing the complete vibrational spectrum of molecular nitrogen.

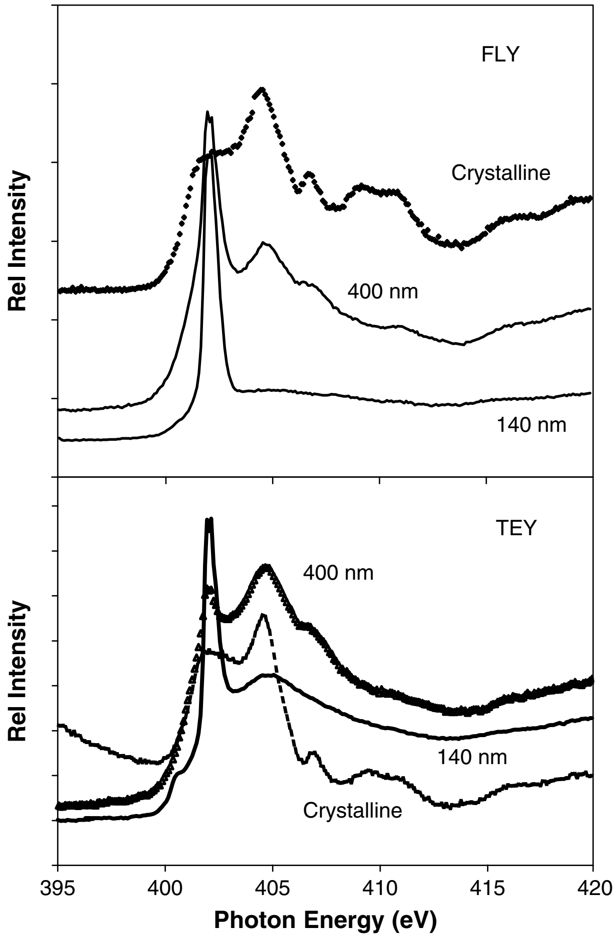

Figure 5. Fluorescence (FLY) and TEY mode spectra of ion-assisted deposited amorphous GaN films 140 and 400 nm thick in comparison with a crystalline sample.

The effect of film thickness was thus examined in the N K edge XANES spectrum and is shown in Fig. 5. Both TEY and fluorescence spectra reveal significant differences in the structure of these films as a function of the respective analytical depths. The thicker films yield spectra much closer to that of the crystalline sample in both the TEY and fluorescence modes. Indeed, the more surface-sensitive TEY spectra of the thick film show a structure very close to that of the crystalline film. This confirms the nature of the duplex structure observed in cross-sectional TEM studies, with a surface layer showing some degree of short-range crystalline structure.

Kasrai *et al*. discuss the relative analytical depth of the TEY and fluorescence spectra for these materials.[14] The conclusion, based on measurements from Si and confirmed with GaN,[15] is that the typical information depths in the TEY and fluorescence spectra are around 5–7 and 70–100 nm, respectively. Thus the zone of increased crystallinity is strongly surface located and, more importantly, is barely found at all in films of less than ~150 nm in thickness. The conclusion is that the most amorphous films are the thinnest and this is associated with significant amounts of molecular nitrogen trapped in the films. The origin of this effect is not clear but it is possible that the nitrogen concentrates in the more disordered region close to the substrate interface, which may also correspond to the region with the highest levels of residual oxygen. This hypothesis is currently being examined.

CONCLUSIONS

X-ray absorption near-edge spectroscopy has been found to provide an excellent complement to conventional XPS in the analysis of GaN-based semiconductor materials. In particular, the increased sensitivity of the XANES spectrum to changes in chemical environment has been exploited to elucidate the structure of amorphous GaN thin films deposited by IAD methods.

X-ray amorphous TEM studies had suggested that these materials displayed zones of microcrystallinity, particularly in the near-surface region of films >150 nm thick, thus the nature of the local bonding and the geometry were of interest. The positions of transitions observed in the N K near-edge spectra were entirely consistent with assignments in the band structure calculations of others,[10] but revealed major differences in coordination and geometry around the nitrogen. Films of up to 150 nm thick displayed a spectrum dominated by the single transition at 402 eV, widely attributed to an sp^2-type environment[11,12] but in this work was resolved to be molecular nitrogen. Thicker films displayed a layered structure, where the surface region more closely resembled the structure of crystalline GaN. The differing analysis depths of the TEY and less-surface-sensitive fluorescence yield spectra were especially useful in confirming the nature of this layered structure. The cause of the molecular nitrogen accumulation at the substrate interface is the subject of further investigation.

Acknowledgements

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