

NEXAFS Study of Film Orientation on Optical Fibres

Single source Chemical Vapour Deposition (CVD) provides a simple and relatively inexpensive method of producing semiconductor thin films for device applications. While it is possible to grow thin films with a variety of crystallographic structures, usually only a very specific set of properties are acceptable for device applications. In most cases the films in question must be highly crystalline with a single crystallographic orientation. Obtaining thin films with these properties is not always achievable at the outset, especially when aspects of the technique, equipment or precursor are novel. While X-ray Diffraction has been traditionally used to characterise the crystallographic properties of thin films, this technique has specific limitations. Two examples are given below of the use of angle dependent NEXAFS analysis as a complementary technique in providing insights into the crystallographic structure and growth processes in thin films.

The all fibre acoustooptic modulator offers great potential in the area of telecommunications. A vital component of this device is a piezoelectric thin film located around the circumference of the optical fibre. In order for the film to generate a net piezoelectric response, the film must possess a single c-axis crystallographic orientation.

Determining the crystallographic orientation of a thin film grown on a planar substrate such as a silicon wafer is a relatively simple task with XRD. Unfortunately the same cannot be said when the film is grown on an optical fibre. The differences between XRD on a planar substrate and on a fibre are shown in Figure 1. The dark head arrows indicate the direction of the c-axis that is perpendicular to the substrate. For the planar film, the angle of the incident x-rays (solid arrows) satisfy the Bragg condition for the c-plane of the crystal. The outgoing x-rays (dotted arrows) are collected by the detector. Since all the crystallites of the film have the same c-axis orientation with respect to each other, this results in reflections for the c-plane and no other.

In the case of optical fibres the crystallites in the films are c-axis oriented with respect to a localised region of the substrate. Since the substrate is curved, the c-axis of the crystallites from different parts of the film will diffract differently. As a result there will always be a small number of crystallites that will satisfy the Bragg condition. The final result will be that the XRD will appear similar to that of a powder.

The anisotropy of ZnO allows angle dependent NEXAFS to be performed. In ZnO the Zn and O atoms are tetrahedrally coordinated with sp^3

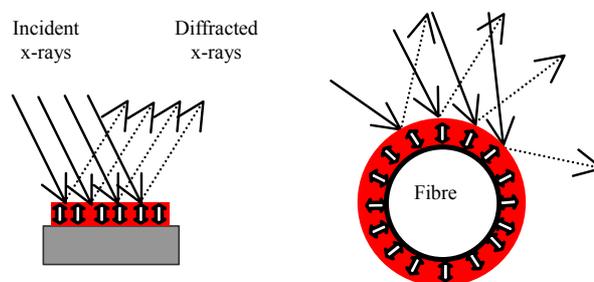


Fig. 1: Effect of XRD performed on c-axis oriented films on flat (left) and optical fibre (right) substrates.

hybridisation with the Zn atom at the centre, there are four oxygen atoms bound to the zinc, three of these are located roughly in an a, b plane with the fourth located directly above the zinc atom. A $1s \rightarrow 4sp^3$ transition can promote the electron to any of the four empty states located in the direction of the coordinating oxygen atoms.

ZnO does not possess identical bonds in all four directions. The length of the Zn-O bond in the c-axis direction is longer than the Zn-O bonds in the a, b plane. As a result of this, a $1s \rightarrow 4sp^3$ transition to the empty state in the c-axis will occur at a different energy from a $1s \rightarrow 4sp^3$ transition to the empty states in the a, b axes.

Figure 2a shows the difference between a $1s \rightarrow 4sp^3_{(c-axis)}$ transition and the $1s \rightarrow 4sp^3_{(a,b)}$ transition for a c-axis oriented zinc oxide film on a planar substrate at two different angles relative to the x-ray beam.

The pre-edge at ~ 9663 eV of the normal incident spectrum was attributed to $1s \rightarrow 4sp^3_c$ transitions (the dark line in fig. 2), and the main

peak at ~ 9670 eV (the lighter shaded line) was attributed to $1s \rightarrow 4sp^3_{a,b}$ transitions. Comparing this with a 'randomly' oriented film (where peaks from the a, b and c axis reflections were observed in XRD), it is evident that the random film is considerably less angle dependent, as shown in Figure 2b.

However it is interesting to note that the random film in both orientations has a similar lineshape to the pure a, b, spectrum of the c-axis film. This is because in a completely random film the $1s \rightarrow 4sp^3_{a,b}$ transitions outnumber the $1s \rightarrow 4sp^3_c$ transitions 3 to 1.

Hence when a mixture of crystallographic orientations is present, the NEXAFS spectra will resemble the pure a, b spectrum. However the main peak at ~ 9670 eV is reduced compared to that of the pure a, b spectrum. This is due to the spectrum being averaged with the $1s \rightarrow 4sp^3_c$ transitions.

When angle dependent NEXAFS is performed on a film grown on a fibre, there are two positions where the greatest angle dependency occurs; when the fibre is mounted horizontally and vertically with respect to the x-ray polarisation, as shown in Figure 3.

In Figure 3a, the c-axis of the crystallite is depicted as a black line. For a c-axis oriented film, the c-axis of the ZnO crystal is located perpendicularly to the substrate. In parallel orientation the electric field component of the x-ray polarization is perpendicular to the c-axis in all areas around the fibre. The resulting spectrum will resemble the normal incidence spectrum for the planar reference film with a strong emission at ~ 9670 eV. By contrast, in perpendicular orientation, the $1s \rightarrow 4sp^3$ transitions occur in all three axes resulting in a NEXAFS spectrum where the absorption at ~ 9670 eV is reduced compared to that of the pure $1s \rightarrow 4sp^3_{a,b}$ NEXAFS spectrum.

However if the film has a, b orientation (where the c-axis of the crystallites are parallel to the substrate), the effect is somewhat different. In Figure 3b the distribution of the c-axis has been depicted with a darkened disc. The a, b axis distribution of the molecular orbitals is essentially three dimensional. Thus for all regions of the film around the fibre both the $1s \rightarrow 4sp^3_{a,b}$ and the $1s \rightarrow 4sp^3_c$ transitions will occur. In contrast, there is a section of the film for perpendicular orientation where the $1s \rightarrow 4sp^3_c$ transition is minimised. This difference will result in a stronger emission at ~ 9670 eV since the resulting spectrum will more closely resemble the planar reference film at normal incidence.

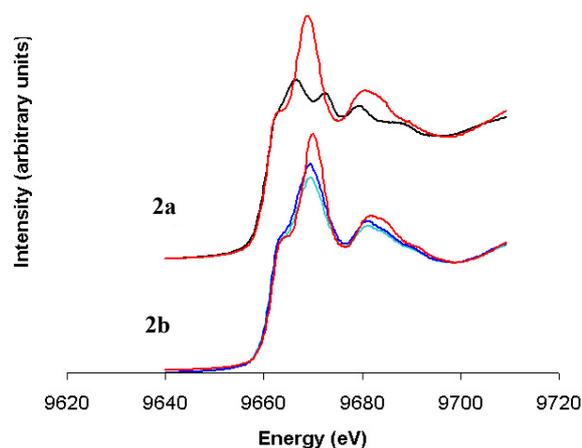


Fig. 2: Zn K-edge angle dependent NEXAFS of a Zinc Oxide film on a planar substrate: top a c-axis reference film and 2b) a randomly oriented film.

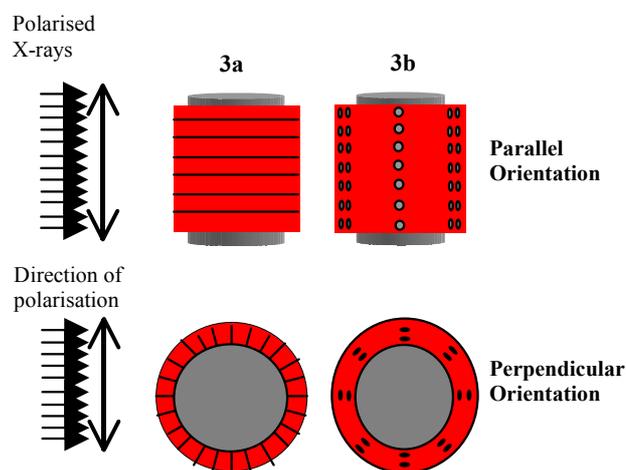


Fig. 3: Interactions between x-rays due to positions of fibre relative to x-ray polarisation for a: 3a) c-axis oriented film and 3b) an a, b-oriented film.

Angle dependent NEXAFS was performed on ZnO films grown at a variety of substrate temperatures ranging from 350°C to 500°C . The two extremes are shown in Figure 4.

For films grown at 350°C the difference in peak height between the perpendicular and parallel orientations was $\sim 1\%$. This indicated the films grown at this temperature had a completely random orientation. The difference in peak heights between the two positions increased with increasing growth temperature to a maximum of $\sim 10\%$ for films grown at 500°C . This indicated the films were a, b oriented rather than c-axis oriented. This was attributed to temperature differences in the heating of planar substrates compared to the fibres.

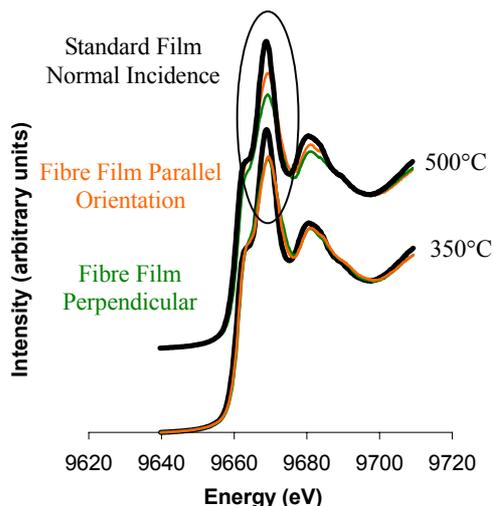


Fig. 4: Zn K-edge angle dependent NEXAFS of films on fibers at 350 and 500°C

While c-axis oriented films were not obtained, this technique nevertheless demonstrated that it is possible to use angle dependent NEXAFS to determine the crystallographic orientation of thin films on optical fibres.

Oxygen is a common impurity within GaN thin films deposited from the CVD process. The oxygen residues, originating either from the precursors or from the vacuum environment, can incorporate into the bulk structure rather than segregate at the grain boundary. The crystallographic properties of the films are therefore dependent on the concentration of the oxygen incorporation. NEXAFS has been used to study the correlation of the oxygen concentration and level of crystallinity within the films.

Figure 5 shows the N *K*-edge and Ga *L*₃-edge NEXAFS spectra of the GaN polycrystalline standard at normal and grazing conditions. The N 1s absorption edge was recorded at 402.7 eV. The significance of the angular dependency concerns the increased intensity of the peaks at 404.8 eV and 406.8 eV. According to the dipole selection rule, the N 1s electrons will be promoted to the nearest empty *p* states. Since information concerning the orbitals perpendicular to the film surface will be maximised at grazing incidence, the peaks at 404.8 eV and 406.8 eV were related to the transitions between 1s → 2*p*_{*x,y*} and 1s → 2*p*_{*z*} orbitals, respectively.

The molecular structure of hexagonal GaN consists of slightly distorted GaN₄ tetrahedra with three Ga-N bonds involving the hybridised 2*p*_{*x,y*} orbitals (in-plane bonds), and a slightly longer bond

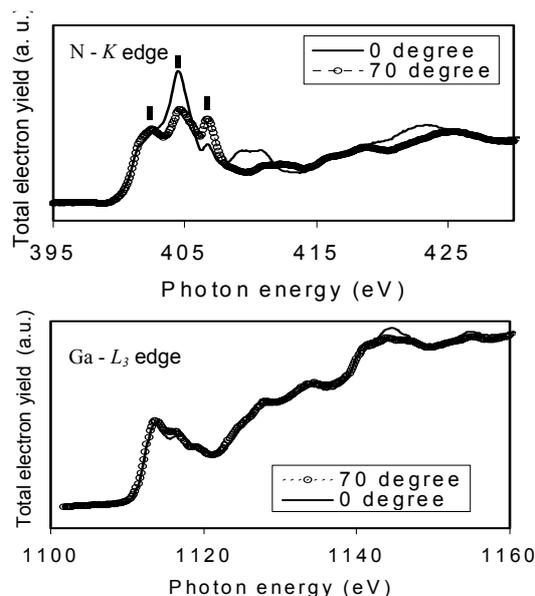


Fig. 5: N *K*-edge and Ga *L*₃-edge NEXAFS spectra of GaN reference at grazing and incident conditions

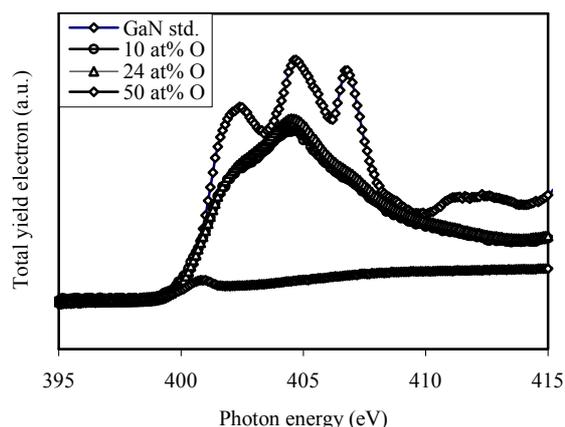


Fig. 6: N *K*-edge NEXAFS spectra of GaN reference and thin films with varying oxygen concentration

involving the hybridised 2*p*_{*z*} orbitals (out-of-plane bond), parallel to hexagonal (002) direction. The observed angular dependency during N *K*-edge measurements indicated that the GaN reference was oriented preferentially along the hexagonal (002) direction. In addition, the relative intensity of the peak at 404.8 eV directly monitored the concentration of the in-plane bonds, while the intensity of the 406.8 eV peak monitored the out-of-plane bonds. In contrast, the Ga *L*₃-edge transitions were virtually independent of the incident angle, as the spectra mainly concerned the electronic transitions to the unoccupied *s* valence states.

Figure 6 shows the N *K*-edge grazing incident NEXAFS normalised spectra of the oxygen-

nated GaN films and the reference standard. For the crystalline films with oxygen lower than 25 at%, the absorption edge and the in-plane components were recorded at 402.7 and 404.8 eV respectively, similar to that of the standard. The intensity of the peak attributed to the out-of-plane components was decreased dramatically relative to that of the reference and was not well resolved. In particular, the spectra show the presence of a broad shoulder at the energy range between 405 - 410 eV. These results indicated that oxygen preferentially substituted the out-of-plane components of GaN₄ tetrahedra. Such substitution is energetically favoured as the (002) plane has the lowest surface free energy similar to that of the hexagonal zinc oxide. For the amorphous film with oxygen concentration ~50 at%, the absorption edge was shifted to a lower energy of 401.1 eV, while the out-of-plane and in-plane peaks were not well defined. This indicated that the corresponding out-of-plane and in-plane components of GaN₄ tetrahedra were substituted by oxygen.

BEAMLINES

24A Wide Range beamline, NSRRC
20B Photon Factory, Tsukuba, Japan

EXPERIMENTAL STATION

Surface-interface end station

AUTHORS

E. Lee, N. Tran, J. Russell, and R. Lamb
School of Chemistry, University of NSW, Sydney,
Australia

L. Lai and Y. Yang
National Synchrotron Radiation Research Center,
Hsinchu, Taiwan

PUBLICATIONS

- E. Lee, N. Tran, J. Russell, and R. Lamb, *J. Appl. Phys.* **92**(6), 2996 (2002).
- N. Tran, W. Holzschuh, R. Lamb, L. Lai, and Y. Yang, *J. Phys. Chem. B* **107**(35), 9256 (2003).
- N. Tran, R. Lamb, L. Lai, and Y. Yang, *J. Phys. Chem. B* (2004), submitted.

CONTACT E-MAIL

r.lamb@unsw.edu.au