

## Influence of Oxygen on the Crystalline–Amorphous Transition in Gallium Nitride Films

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Oxygen is a common impurity in nitride-based materials that affects the properties of technologically important materials such as gallium nitride semiconductors. In this work, the influence of oxygen on the structural evolution of GaN films is investigated using near-edge X-ray absorption fine structure (NEXAFS). The combined spectra of Ga  $L_3$ -edge, N K-edge, and O K-edge indicate that the gallium coordination, formed by a mixture of oxide and nitride bonds, is directly dependent on the concentration of oxygen in the films. Below 24 atom % oxygen, gallium atoms are tetrahedrally coordinated within the films, while at higher concentrations the octahedral environment persists.

## Introduction

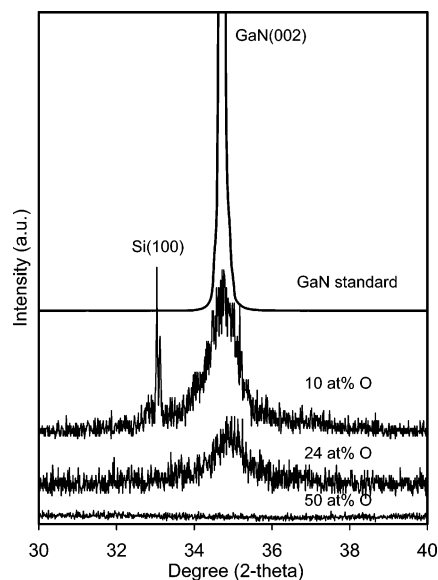
Crystalline thin films of gallium nitride semiconductor have been utilized in a variety of modern light-emitting devices. These films can be routinely grown using the low-pressure methods such as chemical vapor deposition or molecular beam epitaxy. During growth, the residual oxygen from the less than perfect vacuum environments is easily incorporated into such films. Thermodynamically,<sup>1</sup> this reflects the preferential reactions of oxygen rather than nitrogen with gallium atoms, resulting in a more stable Ga–O species.<sup>2</sup>

We are interested in the influence of oxygen on the crystallographic structures of gallium nitride thin films formed by low-pressure chemical vapor deposition. Theoretical and experimental studies have suggested that GaN can incorporate up to ~30% oxygen while retaining its wurtzite (hexagonal) structure.<sup>3</sup> This is consistent with our experiments for oxygen concentration up to ~24%. The results also suggest that there is a decrease in the average crystallite sizes (Figure 1). This can be explained by the formation of oxygen and gallium neutral complexes, which segregate at the grain boundaries and consequently inhibit the nucleation.<sup>4</sup>

In this paper, we examine how the incorporation of oxygen modifies the local structural order within GaN thin films grown using single source precursors. This low-energy deposition process is ideally suited to a detailed investigation of the Ga atomic environment. We utilize the short-range, near-edge X-ray absorption fine structure (NEXAFS) technique and the FEFF8 multiple-scattering calculations to study the film local structures.<sup>5</sup>

## Experimental Procedures

The polycrystalline GaN films were grown on Si(100) substrates using chemical vapor deposition of the single source precursor  $(\text{CH}_3)_3\text{Ga}\text{N}_3$ .<sup>6</sup> Deposition was carried out in a high-vacuum chamber with a background pressure of  $\sim 4 \times 10^{-7}$

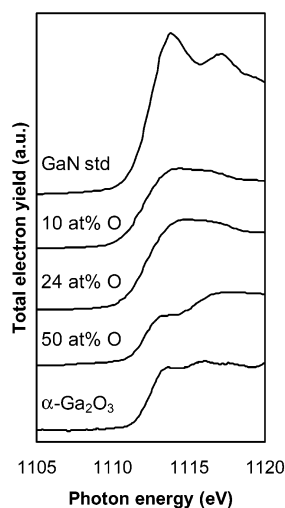


**Figure 1.** X-ray diffraction patterns of the hexagonal GaN(002) reference and thin films with varying oxygen concentration. In the XRD of the film with ~10 atom % oxygen, the doublet at  $2\theta \sim 33^\circ$  was attributed to the underlying Si(100) substrate, and its intensity was dependent on the alignment of Si in the diffractometer.

Torr. The partial pressure of the precursor was  $\sim 5 \times 10^{-5}$  Torr during growth. The oxygen content of the films originated from the vacuum environment and was controlled by variation of the substrate temperature during precursor deposition. From 400 to 600 °C, oxygen concentration within films decreased from ~50 to 10 atom %.

The chemical composition within the films was examined using a Kratos XSAM800 X-ray photoemission spectrometer (XPS) with an unmonochromated Mg  $K\alpha$  source.<sup>1</sup> X-ray diffraction (XRD) was performed using a PW 3040/60 X'Pert Pro Diffractometer with a Cu  $K\alpha$  source. The near-edge X-ray absorption fine structure experiments were carried out at beamline 24A, National Synchrotron Radiation Research Centre, Hsinchu, Taiwan. For the multiple-scattering FEFF8 calcula-

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**Figure 2.** Ga  $L_3$ -edge absorption spectra of GaN reference, thermally stable  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> reference, and GaN thin films with varying oxygen concentration.

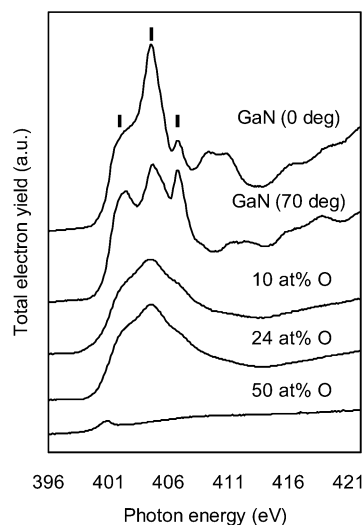
tions, the input parameters were generated by ATOMS.<sup>7</sup> The self-consistent field potential was calculated within a cluster size of 4 Å. The exchange potential of Hendin–Lundqvist models was used, and the cluster size for full multiple-scattering calculations was approximately 6 Å.

## Results and Discussion

The XRD patterns in Figure 1 indicate that GaN films with the oxygen concentration lower than ~24 atom % are preferentially oriented along the hexagonal (002) direction perpendicular to the substrate surface. The (002) peak in the films with oxygen of ~10 atom % is detected at  $2\theta \sim 34.7^\circ$ , similar to that of the hexagonal GaN(002) reference. This peak shifts to  $2\theta \sim 34.9^\circ$  as the oxygen concentration increases to ~24 atom %. The relatively small increase of  $2\theta$  values suggests the presence of the residual stress within the bulk of the film. Formation of stress is attributed to the volume expansion due to the incorporation of oxygen during film growth. By ~50 atom %, the film is considered amorphous.

These XRD results can be explained in terms of the local structural rearrangements that involve the Ga–O and Ga–N species. In particular, the hexagonal phase of GaN consists of slightly distorted GaN<sub>4</sub> tetrahedral units. In contrast, Ga<sub>2</sub>O<sub>3</sub> remains in a variety of crystallographic phases defined by the coordination of Ga atoms. In the low-temperature, metastable phases, Ga atoms are distributed between the tetrahedral and octahedral coordination. In the thermally stable phase, Ga atoms remain octahedrally coordinated. The interdependency between the coordination and crystallographic structures of Ga<sub>2</sub>O<sub>3</sub> is similar to that of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) compounds.<sup>8</sup>

To investigate this in detail, we have used Ga  $L_3$ -edge NEXAFS measurements to examine the local structures of these GaN films.<sup>9–11</sup> In the energy range from ~1110 to 1120 eV, the Ga  $L_3$ -edge spectrum of the GaN reference exhibits a key absorption edge together with peaks at ~1113 and ~1117 eV (Figure 2). The spectrum arises from the electronic transition to the s-hybridized orbital and partly to the d-hybridized orbital. This is confirmed by our FEFF8 calculations of the density-of-state (DOS) projected onto gallium atoms. The Ga  $L_3$ -edge measurements for the films with oxygen concentration from 10 to 24 atom % result in a broad peak within the above energy range (Figure 2). The XRD patterns indicate that these films have hexagonal (002) structure, suggesting that the Ga-

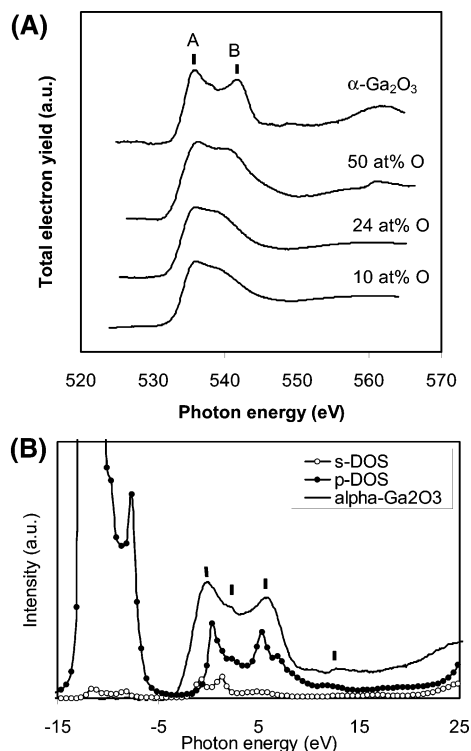


**Figure 3.** N K-edge adsorption spectra of GaN reference and thin films with varying oxygen concentration. The spectra of the reference were recorded at the normal and grazing incident conditions with the angles between the X-ray beam and sample surface normal being at  $0^\circ$  and  $70^\circ$ , respectively. The spectra of the films were recorded at  $70^\circ$ .

tetrahedral structures remain intact. However, the NEXAFS spectra are not well defined. These combined results show that the oxygen incorporation modifies slightly the GaN<sub>4</sub> units in these films. These modified tetrahedral structures are formed via the gallium oxide–nitride (oxynitride) components. For this, tetrahedron is the common form in all metastable gallium oxide compounds, and there is only a slight difference between the atomic distance of Ga–O (1.82 Å) and Ga–N (1.94 Å).<sup>12,13</sup> The measurements for the film with oxygen concentration of ~50 atom % result in a doublet separated by ~3 eV, similar to that of the thermally stable  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> reference. Therefore for this film, it is suggested that Ga atoms are remain primarily within the octahedral structure.

Formation of the Ga-tetrahedral structure from the oxynitride can be confirmed using angle-dependent N K-edge NEXAFS (Figure 3).<sup>1</sup> For the GaN reference, the N 1s absorption edge is recorded at 402.7 eV. The significance of the angular dependency concerns the intensity enhancement of the peaks at 404.8 and 406.8 eV, as the measurements are carried out at normal and grazing incidence, respectively. The peak intensity at 402.7 eV is also slightly enhanced at grazing incidence. The N K-edge spectra are related to the transition of N 1s electrons to the nearest empty p states. Since information concerning the orbital perpendicular to the film surface will be maximized at grazing incident geometry, the peaks at ~404.8 and 406.8 eV are therefore related to the transitions from  $1s-2p_{x,y}$  and  $1s-2p_z$  orbital, respectively.<sup>9–11,14</sup> The tetrahedral GaN<sub>4</sub> units are formed by three Ga–N bonds involving the hybridized  $2p_{x,y}$  orbital (in-plane bonds) and a slightly longer bond involving the hybridized  $2p_z$  orbital (out-of-plane bond), parallel to the (002) direction. The relative intensity of the peak at ~404.8 eV therefore directly monitors the concentration of the in-plane bonds, while the intensity of the ~406.8 eV peak monitors the out-of-plane bonds.

For the grazing-incidence spectra of the films with oxygen concentration from 10 to 24 atom %, the intensity of the peak attributed to the out-of-plane components is decreased dramatically and is not well resolved. In particular, these spectra show the presence of a broad shoulder at the energy range between 405 and 410 eV. These results indicate that oxygen preferentially substitute the out-of-plane components of GaN<sub>4</sub> tetrahedra. Such

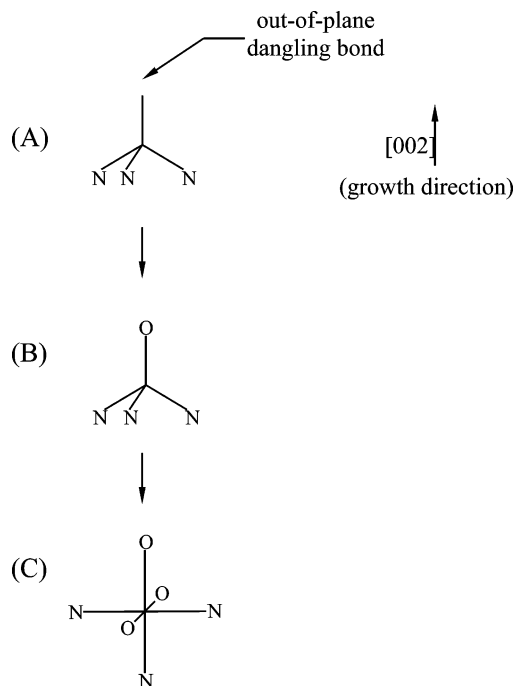


**Figure 4.** (A) O K-edge spectra of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> reference and GaN thin films with varying oxygen concentration. (B) FEFF8 calculations of the density-of-state projected on oxygen atoms and the measured O K-edge spectrum of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> reference.

substitution is energetically favored as the (002) plane has the lowest surface free energy, similar to that of hexagonal zinc oxide.<sup>15</sup> For the amorphous film with oxygen concentration  $\sim 50$  atom %, the absorption edge is shifted to a lower energy of  $\sim 401.1$  eV. In addition, the out-of-plane and in-plane peaks are not well defined. This confirms that the GaN<sub>4</sub> tetrahedra have been modified in the amorphous film.

The formation of the Ga-octahedral structure in the film with oxygen concentration of  $\sim 50$  atom % can also be confirmed from the O K-edge absorption spectra (Figure 4A). In particular, the O K-edge spectrum of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> reference shows a doublet, including the absorption edge at 535.4 eV (peak A) and an additional peak at 540.7 eV (peak B). Figure 4B shows the FEFF8 calculations of the DOS projected on oxygen atoms within the GaO<sub>6</sub> octahedral structure. During the calculations, peaks A and B are reproduced. The calculated results also show that these peaks are predominantly related to the transition of 1s electrons to the *p*-hybridized orbital. The hybridization may involve the 3d and 4s orbital of gallium atoms, as this has been shown in the Ga L<sub>3</sub>-edge spectra above. For the film with oxygen concentration of  $\sim 50$  atom %, the two main peaks in the spectrum of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> are reproduced during the O K-edge measurements. However, peak B is relatively broad compared to that of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> spectrum. Furthermore, this peak is not well defined in the absorption spectra for the films with oxygen concentration lower than  $\sim 24$  atom %. The O K-edge spectrum of the film with  $\sim 50$  atom % oxygen confirms the Ga L<sub>3</sub>-edge result, which suggests the presence of the distorted Ga-octahedral structures in this film. The distorted octahedral structures could only be formed via the gallium oxynitride components.

We have previously suggested that the Ga-tetrahedral structure remained intact during oxygen incorporation into the films.<sup>1</sup> The above results facilitate the formation of a structural model in which the coordination of Ga atoms is dependent on the



**Figure 5.** Schematic of the interactions of oxygen with the GaN<sub>4</sub> tetrahedral structure. (A) Growth of gallium nitride tetrahedral structure along the (002) direction. (B) At relatively low oxygen concentration, interactions of oxygen with the out-of-plane dangling bond leads to formation of the gallium oxynitride tetrahedra. (C) Increase of oxygen incorporation leads to formation of the gallium oxynitride octahedra. Formation of the tetrahedral GaO<sub>4</sub> structure is excluded in this model.

atomic concentration of oxygen (Figure 5). The model consists of a growing Ga-tetrahedral unit with three in-plane Ga–N bonds and an out-of-plane dangling bond parallel to the (002) axis (Figure 5A). This corresponds to the ...ABAB... stacking sequence.

For the films with an oxygen incorporation lower than approximately 25 atom %, an oxygen atom will form an out-of-plane Ga–O bond, leading to formation of the GaN<sub>3</sub>O tetrahedral structure (Figure 5B). This is supported via the above N K-edge results. Previous studies have also suggested that the structural defects within GaN, formed by the oxygen incorporation, preferentially grow along the (002) direction.<sup>16,17</sup> This model is also consistent with the long-range XRD measurements, where the films with lower than 24 atom % oxygen are (002) oriented (Figure 1). It is expected that formation of the GaN<sub>3</sub>O structures will not greatly influence the bulk structure and result in formation of the well-defined (002) hexagonal structure. However, formation of the GaN<sub>3</sub>O structures would lead to the distortion of the bulk, resulting in residual stress within films.

The increase of the oxygen concentration to approximately 50 atom % may lead to a tetrahedral–octahedral transformation within the films (Figure 5C). These films would consist primarily of gallium oxynitride octahedral units effectively looking amorphous in XRD terms. It is interesting to note, however, from the NEXAFS results, there is no evidence of formation of the tetrahedral GaO<sub>4</sub> structure, despite this being a common form in most gallium oxides. The complete substitution from GaN<sub>4</sub> to GaO<sub>4</sub> during oxygen interactions would thus be energetically unfavored.

## Summary

NEXAFS measurements and FEFF8 calculations were carried out to examine the forms of the oxygen impurity within the

hexagonal structure of gallium nitride thin films. The chemical interactions of oxygen with the gallium nitride crystals modify the short-range structures and control the long-range order. This is important in better understanding the influences of oxygen in the gallium-based and nitride-based materials. It is highly likely that the long- and short-range structural evolution in aluminum nitride during interactions with oxygen would follow a similar pathway as that of gallium nitride.

**Acknowledgment.** This work was supported by the Australian Synchrotron Research Program. The authors would also like to thank L. Fan and A. Buckley for their help.

## References and Notes

- (1) The enthalpy of formation of Ga–N and Ga–O bonds is  $-110$  kJ/mol Ga and  $-545$  kJ/mol Ga, respectively. Lide, D. R. *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press: Boca Raton, FL 2002.
- (2) Tran, N. H.; Holzschuh, W. J.; Lamb, R. N.; Lai, L. J.; Yang, Y. W. *J. Phys. Chem. B* **2003**, *107*, 9256.
- (3) Kisailus, D.; Choi, J. H.; Lange, F. F. *J. Mater. Res.* **2002**, *17* (10), 2540.
- (4) Butcher, K. S. A.; Timmers, H.; Chen, A.; P. P.-T.; Weijers, T. D. M.; Goldys, E. M.; Tansley, T. L.; Elliman, R. G.; Freitas, J. A., Jr. *J. Appl. Phys.* **2002**, *92* (6), 3397.
- (5) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. *Phys. Rev. B* **1998**, *58*, 7565.
- (6) Atwood, D. A.; Jones, R. A.; Cowley, A. H.; Atwood, J. L.; Bott, S. G. *J. Organomet. Chem.* **1990**, *394*, C6–C8. Lakhota, V.; Neumayer, D. A.; Cowley, A. H.; Jones, R. A.; Ekerdt, J. G. *Chem. Mater.* **1995**, *7*, 546.
- (7) Ravel, B. *J. Synchrotron Radiat.* **2001**, *8*, 314.
- (8) Levin, I.; Brandon, D. J. *Am. Ceram. Soc.* **1998**, *81*, 1995.
- (9) Chiou, J. W.; Mookerjee, S.; Rao, K. V. R.; Jan, J. C.; Tsai, H. M.; Asokan, K.; Pong, W. F.; Chien, F. Z. *Appl. Phys. Lett.* **2002**, *81*, 3389.
- (10) Katsini, M.; Paloura, E. C.; Moustakas, T. D. *Appl. Phys. Lett.* **1996**, *69*, 4206.
- (11) Lawniczak-Jablonska, K.; Suski, T.; Gorczyca, I.; Chritensen, N. E.; Attenkofer, K. E.; Perera, R. C. C.; Gullikson, E. M.; Underwood, J. H.; Ederer, D. L.; Weber, Z. L. *Phys. Rev. B* **2000**, *61*, 16623.
- (12) Nishi, K.; Shimizu, K.; Takamatsu, M.; Yoshida, H.; Satmusa, A.; Tanaka, T.; Yoshida, S.; Hattori, T. *J. Phys. Chem. B* **1998**, *102*, 10190.
- (13) Downs, A. J. *Chemistry of Aluminium, Gallium, Indium and Thallium*, 1st ed.; Blackie Academic & Professional: Glasgow, 1993. Nakamura, S.; Fasol, G. *The Blue Laser Diode*; Springer-Verlag: Berlin, 1997.
- (14) Lübke, M.; Bressler, P. R.; Braun, W.; Kampen, T. U.; Zahn, D. R. T. *J. Appl. Phys.* **1999**, *86*, 209.
- (15) Tran, N. H.; Hartmann, A.; Lamb, R. N. *J. Phys. Chem. B* **1999**, *103*, 4264 (and refs therein).
- (16) Elsner, J.; Jones, R.; Heggie, M. I.; Sitch, P. K.; Haugk, M.; Frauenheim, T.; Oberg, S.; Briddon, P. R. *Phys. Rev. B* **1998**, *58*, 12571.
- (17) Elsner, J.; Jones, R.; Haugk, M.; Gutierrez, R.; Frauenheim, T.; Heggie, M. I.; Oberg, S.; Briddon, P. R. *Appl. Phys. Lett.* **1998**, *73*, 3530.