

Quantitative study of molecular N₂ trapped in disordered GaN:O films

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The structure of disordered GaN:O films grown by ion-assisted deposition is investigated using x-ray absorption near-edge spectroscopy and Raman spectroscopy. It is found that between 4 and 21% of the nitrogen in the films is in the form of molecular N₂ that interacts only weakly with the surrounding matrix. The anion to cation ratio in the GaN:O host remains close to unity, and there is a close correlation between the N₂ fraction, the level of oxygen impurities, and the absence of crystalline order in the GaN:O matrix.

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I. INTRODUCTION

Determining the atomic scale structure and the resulting electronic properties of complex material systems is an ongoing challenge in physics research.^{1,2} An especially interesting material with a complex structure is disordered gallium nitride (GaN). It has been predicted that fully amorphous GaN has a well-defined band gap relatively free of in-gap states, and may provide a useful alternative to its crystalline counterpart.^{3,4} However, the amorphous state is not in itself unique, and different fabrication techniques give rise to a range of disordered structures. Experimental studies have shown that the resulting optical and electronic properties depend sensitively on the details of this nanostructure, including the presence of nanocrystallites and impurities.⁵⁻¹⁷

In this paper we report x-ray absorption near-edge spectroscopy (XANES) and Raman spectroscopy results from disordered GaN films containing varying levels of oxygen impurities (GaN:O). Our principal observation is that between 4 and 21% of the nitrogen in these films is trapped as molecular N₂, interacting only weakly with the surrounding solid matrix. We have previously shown that the films grown by this technique range from nanocrystalline, with crystallite size of order 3 nm, to fully amorphous, with the latter structure correlated with larger levels of oxygen impurities.^{6,7} Here we observe also a close correlation between the level of oxygen and the N₂ fraction, and we speculate on the nature of this three-way relationship.

II. EXPERIMENTAL DETAILS

The thin films used in this study were grown by ion-assisted deposition (IAD), where Ga atoms are deposited onto a substrate in the presence of an energetic beam

of nitrogen ions.⁵⁻⁸ The ion energy was typically 500 eV, with a total ion current density of 0.2-0.4 mA/cm² and an overall growth rate of around 0.5 Å/s. The resulting films were between 50 and 1000 nm in thickness. Excellent adhesion was obtained onto a range of substrates, including silicon, quartz glass, carbon glass, mylar, and stainless steel. The substrate temperature remained below 100 °C during growth.

Two separate vacuum systems were used for the film growth, with different base pressures of 5×10^{-9} and 5×10^{-6} Torr. Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA) show that films grown in the latter system contain significant amounts of oxygen, as described below, while films grown with the lowest base pressure have low oxygen content close to the measurement resolution of 1 atomic % (at.%).¹⁸ Elastic recoil detection (ERD) analysis found hydrogen fractions of 0.5 and 7 at.% in two representative films containing 1 and 20 at.% oxygen, respectively. For all samples the carbon impurity content was below 1 at.%. The microstructure and degree of crystallinity of the films was determined by x-ray diffraction (XRD), extended x-ray absorption fine structure (EXAFS), and transmission electron microscopy (TEM). All of the films described here are transparent across the visible and show an absorption edge at around 3.5 eV.^{5,7,9}

Nitrogen K-edge XANES measurements were performed on the Canadian SGM beamline at the Synchrotron Radiation Center, Madison, Wisconsin. The monochromator has a maximum resolution of about 70 meV. Data were taken at normal incidence in both the total electron and total fluorescent yield modes (TEY and TFY) using the specimen current and a channel plate detector, respectively. Both techniques yield similar results, although we focus below on TFY data where the penetration depth is estimated¹⁹ to be 70-100 nm and charging effects are not significant. The Raman data reported here were obtained at room temperature from samples

grown on silicon using a Jobin-Yvon LabRam spectrometer. Excitation came from a 325nm HeCd laser with a focus spot size of about 2 μm , and a power of 1–5mW.

III. RESULTS

In Fig. 1(a) we compare the nitrogen K-edge XANES spectrum from an IAD grown GaN:O sample containing about 8 at.% oxygen with the spectrum from a single crystal *c*-axis oriented wurtzite GaN film (*x*-GaN). The *x*-GaN spectrum has an absorption onset at around 397 eV followed by a series of peaks that can be understood in terms of the *p*-projected calculated density of states of wurtzite GaN.^{20,21} The absorption onset of the IAD grown film also lies at about 397 eV, but unlike the *x*-GaN sample, a large narrow peak centred at 401 eV dominates the spectrum. At higher energies the IAD sample spectrum resembles a much-broadened version of the *x*-GaN spectrum, as expected for these strongly disordered films.

A high-resolution scan over the 401 eV peak reveals that it actually consists of at least five narrow absorption lines, the widths of which are limited by the monochromator resolution [Fig. 1(b)]. Also shown is the XANES spectrum of gaseous molecular nitrogen measured on the same beam-line, showing the vibrational splitting of the $2p$ π_g^* resonance (the energy scale was calibrated using the known location of this peak).²² The similarity in peak positions and relative intensities allows us to attribute the 401 eV peak to the π_g^* resonance of molecular nitrogen trapped within the films.¹⁰ The inset to Fig. 1(b) shows the spectrum of gaseous molecular nitrogen expanded to include the contribution from transitions to high energy Rydberg and multiple-electron excited states that begin at about 406 eV (N_2 absorption data above 406 eV taken from Ref. 23).

The fraction F_{N_2} of the nitrogen held in molecular form varies between samples, as illustrated in Fig. 1(c) by the variation in the relative intensity of the π^* peak (the normalization procedure is described below). Interestingly, the films with the greatest N_2 fraction are those that show the most broadening in the underlying GaN:O absorption spectrum. Structural characterization by XRD, TEM, and EXAFS has indicated that these films are fully amorphous, whereas the films with lower N_2 levels contain crystallites of approximate size 3 nm.⁷ Furthermore, RBS and NRA measurements show that the amorphous films also contain high levels of oxygen, typically greater than 15 at.%, and it may be that a significant oxygen level is essential to stabilize the amorphous structure.

An estimate of the value of F_{N_2} for each sample can be obtained in the following fashion. First, we note that the N_2 makes no contribution to the absorption over the energy range 403–406 eV, so the entire contribution in this window is from the GaN:O matrix. The spectra in Fig. 1(c) have been normalized over this range, resulting in an offset that develops above 406 eV representing the extra absorption due to transitions to high energy states in the trapped N_2 . As expected, the offset is proportional to the intensity of the π^* peak, and thus to F_{N_2} .

At photon energies far above the edge the absorption cross section becomes independent of the bonding environ-

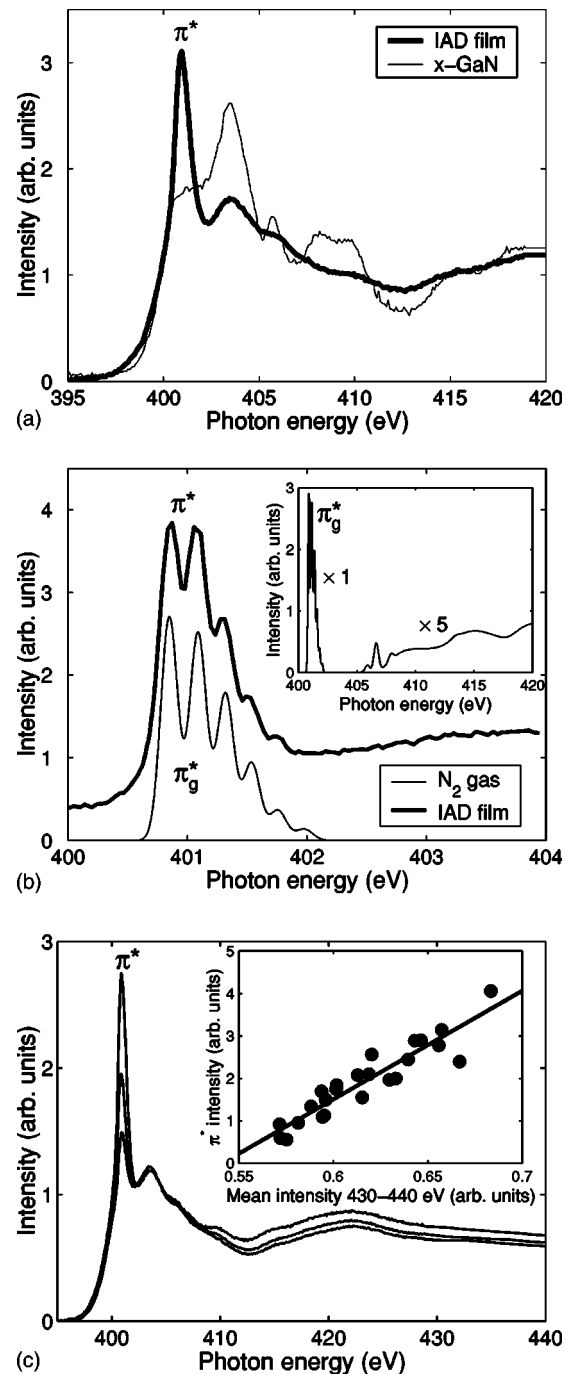


FIG. 1. (a) TFXANES spectra from crystalline GaN and disordered GaN:O. (b) High-resolution π^* and π_g^* resonance spectra from trapped and gaseous N_2 , respectively. Inset: Gaseous N_2 spectrum including contribution from transitions to high energy states (Ref. 23). (c) XANES spectra from several disordered GaN:O films containing differing amounts of trapped N_2 . Inset: π^* absorption versus average absorption between 430 and 440 eV for a series of samples.

ment of the absorbing nitrogen atom. (EXAFS oscillations are of insignificant amplitude here.) Therefore, we examine the energy range 430–440 eV, where there is no evidence of structure in the absorption, and plot the average amplitude in this range against the fitted π^* peak amplitude for each

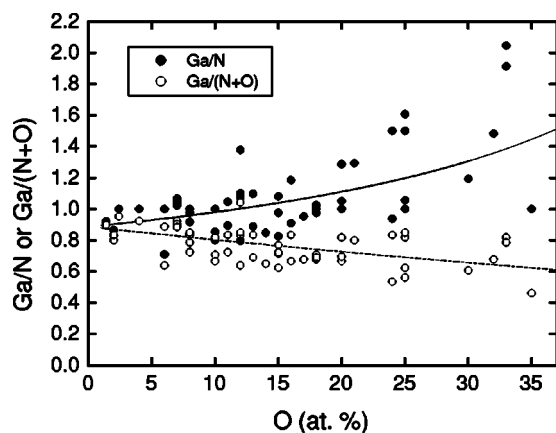


FIG. 2. Measured atomic ratios of gallium to nitrogen (●) and gallium to nitrogen plus oxygen (○), plotted versus the oxygen atomic percentage. The solid and dashed lines show the expected ratios calculated using the N₂ atomic fraction determined from XANES data.

sample [see Fig. 1(c), inset]. Extrapolating these data shows that the absorption between 430 and 440 eV would be about 0.54 (on this scale) in the absence of any N₂. The actual absorption varies from 0.57 to 0.69, so the N₂ contributes between 4 and 21% of the total absorption. Thus we estimate that F_{N_2} varies from 0.04 to 0.21.

It should be noted that the magnitude of the contribution from the GaN:O matrix between 403 and 406 eV depends on the density of *p*-projected electronic states in this range. This in turn may depend on the details of the microstructure, such as the degree of crystallinity. For this reason we chose not to use the *x*-GaN spectrum to estimate the absorption when $F_{N_2}=0$, and instead used only the disordered samples where, apart from the N₂ contribution, there are only subtle variations amongst the spectra. Although the normalization, and hence the value of F_{N_2} , is only approximate, our finding that up to 21% of the nitrogen is in the form of N₂ is consistent with independent estimates described below. We also note that the distinct resonant peaks above 406 eV in the gaseous N₂ spectrum [Fig. 1(b), inset] are not apparent in the offset region of the IAD GaN:O spectra. This is consistent with results from adsorbed films of N₂, where interaction with the substrate usually broadens the resonances into a smooth continuum.^{23,24}

The effect of oxygen incorporation on the stoichiometry, determined by RBS and NRA, is plotted in Fig. 2. The Ga to N ratio tends to increase above unity as the oxygen concentration increases. We attribute this to the substitution of oxygen for nitrogen in the GaN matrix, so that the composition is roughly GaO_{*x*}N_{1-*x*}. There are relatively few reports in the literature on the properties of deliberately grown GaO_{*x*}N_{1-*x*}, although the effect of oxygen impurities on the electronic properties of crystalline GaN continues to be an area of active research.² However, it is known that high levels of oxygen ($x \approx 0.3$) can be substituted into GaN without substantially altering the lattice structure.²⁵ We have found no evidence for the formation of a separate gallium oxide phase in TEM, XRD, EXAFS, or Raman measurements.

It was noted above that F_{N_2} increases with oxygen content, with the minimum value 0.04 corresponding to near

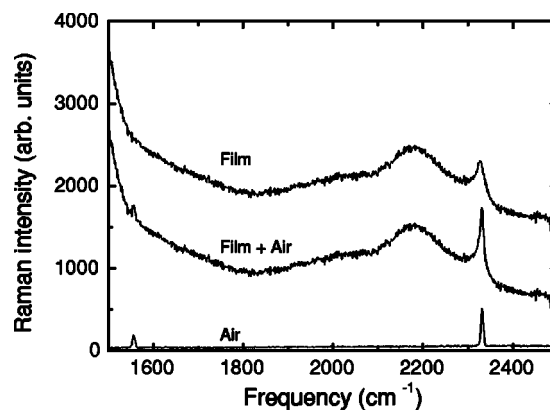


FIG. 3. Raman spectrum from a 130 nm thick film with negligible oxygen content, showing the molecular N₂ vibration at 2330 cm⁻¹, as well as the broad third order GaN mode at 2200 cm⁻¹. The curve labelled “Film” has had the contribution from atmospheric N₂ removed to give only the spectrum of the N₂ trapped in the film.

oxygen free samples and the maximum value 0.21 being obtained when the oxygen content $x=0.35$. Assuming a simple linear dependence we write $F_{N_2}=0.04+0.49x$. The solid and dashed lines in Fig. 2 show, respectively, the variation of the gallium to nitrogen and gallium to total cation (oxygen plus nitrogen) ratios expected given this form for F_{N_2} . The trend in both ratios is captured very well with no free parameters.

To the best of our knowledge there are no specific predictions in the literature regarding the energetics of molecular nitrogen defects in GaN.²⁶ Given our growth technique, and the fact that all of the films contain some N₂, it seems likely that the ion beam simply buries some N₂ during growth. Indeed, TRIM calculations show that the penetration depth of the 500 eV N₂⁺ ions is a few atomic layers. The cause of the correlation between N₂ and oxygen content is less obvious. It is known that interstitial N₂ is formed in TiN and CrN films when N atoms are displaced during surface oxidation.²⁷ A similar oxidation process, taking place as the growth proceeds, may add to the N₂ level in our films. Alternatively, it may simply be that the more disordered structure associated with the high oxygen content films is able to trap more N₂. In any case, we stress that the GaN:O matrix is stoichiometric in the sense that the anion to cation ratio, excluding N₂, is approximately one in all films. This is in contrast to GaN amorphized by heavy-ion bombardment, in which N₂ bubbles form from displaced nitrogen, leaving behind a Ga-rich lattice.²⁸

A portion of the Raman spectrum of a low oxygen (≈ 1 at.%) IAD grown film, showing the broad third order GaN mode at 2200 cm⁻¹, is shown in Fig. 3. For comparison, the spectrum from a single crystal GaN film may be found in Ref. 29. Also apparent is a narrow N₂ vibrational mode at 2330 cm⁻¹, which represents a combination of scattering from N₂ in the film and free N₂ in the air between the sample and the microscope objective. We eliminate the latter by subtracting the signal obtained from a bare silicon substrate, where both spectra are first normalized using the molecular oxygen mode at 1556 cm⁻¹ that originates solely from the air. The resulting spectrum, representing only N₂ in the film,

is also shown in Fig. 3. Note that Raman probes the vibrational splitting of the electronic ground state of N_2 , whereas XANES probes the same vibrationally split anti-bonding π^* state. The Raman peak at 2330 cm^{-1} , which corresponds to about 0.29 eV , is therefore at higher energy than the splitting between the lowest vibrational levels of N_2 observed in XANES (0.24 eV).

The laser spot diameter was about $2\text{ }\mu\text{m}$, so for the confocal Raman microscope the air signal comes from a volume just above the sample of roughly $8\text{ }\mu\text{m}^3$, containing about 1.6×10^8 N_2 molecules. The GaN:O absorption coefficient at 325 nm (10^5 cm^{-1}) allows the beam to probe the top 50 nm of the film.^{7,9} As the trapped N_2 peak has roughly 4 times the area of the peak from N_2 in the air, the probed volume of the film contains approximately 6.4×10^8 N_2 molecules, corresponding to a density of 3.2×10^{21} $N_2\text{ cm}^{-3}$. Using the atomic density of crystalline GaN (8.8×10^{22} at. cm^{-3}) to estimate the density of our films we find that about 3% of the nitrogen is in the form of N_2 . This is in excellent agreement with our estimate of 4% based on the XANES results for this sample.

The width of the trapped N_2 peak is about 30 cm^{-1} , considerably broader than the corresponding value of 10 cm^{-1} for free N_2 , and the broadening is most pronounced on the low energy side. The peak is also shifted to lower energy by about 4 cm^{-1} . The fractional peak width $\Delta\omega/\omega$ is only about 1%, implying that the nitrogen molecules experience a weak, but nonzero interaction with the host matrix. The presence of this interaction suggests that the N_2 probably resides in in-

terstitial sites in the films rather than within voids or cracks.

It is interesting to question whether subsequent film treatments, such as thermal annealing, can influence the trapped N_2 . To this end we have annealed a nanocrystalline sample containing about 10 at.% oxygen at $700\text{ }^\circ\text{C}$ for 30 minutes under flowing nitrogen. After annealing the XANES features related to the GaN:O matrix become somewhat sharper, and the π^* peak decreases in intensity by approximately 20% indicating some loss of N_2 from the film.

In conclusion, we have used a range of experimental probes to characterize a series of highly disordered GaN:O films. A detailed analysis of the data has demonstrated quantitatively the presence of molecular N_2 in the films. An interaction with the host matrix leads to only a small broadening of the N_2 vibrational frequency. Both the atomic-scale structure of the GaN:O and the amount of N_2 depend on the growth conditions, especially the level of oxygen impurities. These results highlight the sensitivity of the properties of such highly disordered materials to small variations in the preparation conditions.

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