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Filled and empty states of disordered GaN studied by x-ray absorption and emission

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X-ray absorption and emission spectroscopies are used to study the effects of short-ranged ordering on the electronic states of disordered GaN. Nanocrystalline samples with crystallites as small as 3 nm exhibit an electronic structure resembling a broadened version of that in crystalline GaN. The electronic structure is even more heavily broadened in amorphous GaN films containing oxygen impurities or excess gallium. The oxygen containing films show an additional peak in the density of states just above the conduction band edge, and a downward shift of the valence band edge. The signature of molecular nitrogen trapped within the films is evident in both the absorption and emission spectra. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1782270]

The electronic structure of solids depends sensitively on the arrangement of the constituent atoms. If long-range order is absent, as in the nanocrystalline or amorphous state, the details of the electronic structure are determined by the exact nature of the short-ranged bonding configuration, including specific bonding defects and impurities. Calculating the electronic states of disordered materials is a formidable challenge, so it is of interest to investigate experimentally the evolution of the electronic structure as a system progresses from crystalline through to nanocrystalline and to fully amorphous.

An especially interesting candidate for such a study is GaN. Crystalline GaN (x-GaN) possesses a wide band gap (3.4 eV) making it useful for short wavelength optoelectronic applications. Surprisingly, the optoelectronic properties of GaN are relatively insensitive to crystalline defects.[1] In fact, theoretical studies have indicated that even amorphous GaN (a-GaN) may possess a well-defined wide band gap, and is thus a potential substitute for the more expensive crystalline form.[2] Experimental investigations support this prediction, with several studies reporting optically transparent and photoconductive a-GaN or nanocrystalline GaN (nx-GaN).[3–12] We present a synchrotron radiation study of the filled and unfilled electronic states in disordered GaN films. The measured electronic structure is found to be sensitive to the level and type of disorder, and includes additional features related to the presence of molecular nitrogen trapped within the films.

The disordered GaN films 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.[3] The structure and composition of the samples were determined by x-ray diffraction, transmission electron microscopy, extended x-ray absorption fine structure, and Rutherford backscattering spectroscopy. Data from five separate IAD grown samples, denoted A–E, are presented in this paper. Samples A and D are nanocrystalline, with crystallite size ≈ 3 nm, while samples B and E are amorphous. The latter contain around 20 at. % oxygen impurities, and it appears that the oxygen is essential to stabilize their amorphous structure.[4] Both the nanocrystalline and amorphous films contain trapped N_2 molecules, but have otherwise near equal atomic fractions of gallium and nitrogen plus oxygen.[4] No evidence has been found for a separate gallium oxide phase in any of the measurements. Sample C, which also has an amorphous structure, contains $\approx 15\%$ excess gallium due to the use of a relatively low ion energy during growth (100 eV versus 500–700 eV for the other samples).[3] The gallium rich sample is optically opaque, while the other films are transparent across the visible spectrum.

Nitrogen K-edge x-ray absorption near edge spectroscopy (XANES) was undertaken on the Canadian SGM beamline at the Synchrotron Radiation Center, Madison, Wisconsin. Data were recorded in both fluorescent and electron yield modes, although below we focus on the fluorescent yield data due to the absence of a strong background

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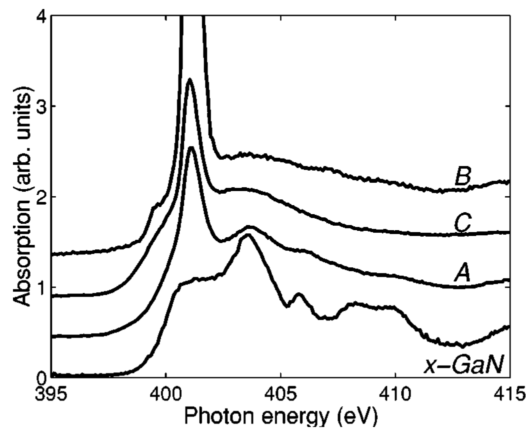

FIG. 1. XANES spectra of samples *A* (nx-GaN), *B* (a-GaN), *C* (Ga-rich), and a reference crystalline GaN film. Spectra offset for clarity.

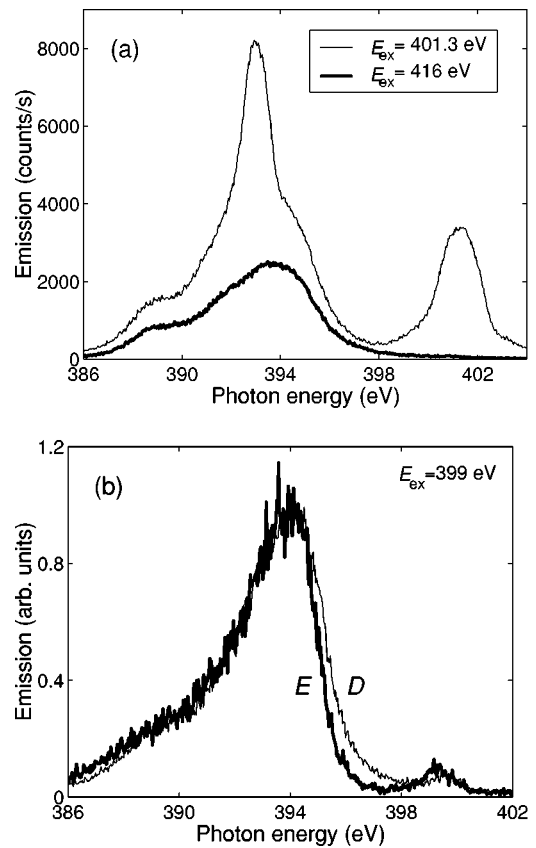

FIG. 2. (a) XES spectra from sample *A* recorded with 401.3 eV and 416 eV excitation. The 401.3 eV excitation is resonant with N_2 trapped within the sample. (b) Comparison between XES spectra of samples *D* (nx-GaN) and *E* (a-GaN).

signal in this measurement. The spherical grating monochromator gave an energy resolution of 70 meV. Nitrogen K-edge x-ray emission spectroscopy (XES) results were obtained at the BESSY U41-PGM beamline. The incident beam energy resolution was around 0.6 eV, and the spectrometer resolution around 1 eV. The energy scale of the SGM beamline data was adjusted so that features in the absorption spectra matched those in comparable measurements from the BESSY beamline.

XANES spectra from samples *A*, *B*, and *C*, and from an epitaxially grown crystalline GaN reference film are compared in Fig. 1. The spectra from the IAD grown films are dominated by a narrow peak at 401 eV, which we have previously shown is the π^* resonance of the molecular nitrogen trapped within the films.[4] At energies above the π^* resonance the spectrum of the nanocrystalline sample *A* is essentially a broadened version of the x-GaN spectrum. Over the same energy range sample *B* shows an even greater degree of broadening than sample *A*. This is consistent with its amorphous structure, which possesses a similar tetrahedral local bonding configuration to x-GaN, but little order beyond a few nearest-neighbor distances.[5]

The absorption onsets of both the nanocrystalline and amorphous samples lie at a similar energy to that of the x-GaN film, although a detailed comparison is difficult due to the nearby π^* peak. Nevertheless, there is no substantial broadening of the edge by the disorder in either case. The amorphous sample *B* also shows a small peak at $\approx$399.5 eV that is not present in the spectra of the nx-GaN or x-GaN samples. The origin of this peak is uncertain at present, although its narrow width ($\sim$0.5 eV) suggests it is related to a localized defect state that appears in the amorphous structure. A peak observed at similar energy in ion-bombarded GaN films has been attributed to states introduced by interstitial nitrogen atoms,[13,14] although this is based on the assumption that the peak lies *below* the conduction band minimum. Comparisons between experimental data and theoretical band structure calculations suggests that the conduction band edge lies around 6 eV below the largest peak in the x-GaN absorption spectrum.[15,16] This places it at 398 eV in Fig. 1, so the 399.5 eV peak actually lies *above* the conduction band edge. There are numerous possible point defects that introduce states above the conduction band edge in GaN,[17] and the presence of oxygen impurities likely extends the possibilities. The formation of such defects is not unlikely under the nonequilibrium growth conditions used here.

The spectrum of the gallium rich sample *C* also shows very little fine structure, consistent with its amorphous nature. Relative to the other samples this gallium rich film also shows enhanced absorption in the energy range just above the absorption edge, which we believe results from states associated with gallium-gallium homopolar bonds. The fact that such defects affect the nitrogen edge XANES provides evidence that the excess gallium substitutes into the lattice rather than forming isolated gallium metal inclusions.

We now focus on XES measurements, which provide complementary information to XANES on the filled electronic levels. The lower curve in Fig. 2(a) shows an emission spectrum from sample *A*, recorded using an excitation energy E_{ex} of 416 eV. Although the valence band peak at 394 eV is slightly broader, the overall shape of the spectrum is very similar to that observed in x-GaN,[16,18,19] implying that the disorder has only a minor effect on the valence band structure in the nanocrystalline films.

The upper curve in Fig. 2(a) shows a spectrum from sample *A* recorded with E_{ex}=401.3 eV. The overall emission intensity is greater than for the E_{ex}=416 eV spectrum due to the greater absorption cross section at this excitation energy. The E_{ex}=401.3 eV spectrum also displays additional features

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related to resonant excitation of molecular nitrogen in the film. The strong elastic peak at 401.3 eV is due to the same N_2 π^* resonance described above in terms of the absorption spectrum. The narrow peak at 393 eV, superimposed on the GaN valence band emission, can be attributed to the $3\sigma_g$ bonding orbital of N_2,[20] observable only when the excitation is resonant with the N_2 absorption. It is possible that interaction with the GaN matrix could alter the symmetry of the N_2 molecules and allow transitions from the nearby $1\pi_u$ and $1\sigma_u$ levels. However, within the experimental resolution used here, there is no clear evidence for such effects. This is in agreement with our previous observations based on Raman spectroscopy, which found only minor broadening of the nitrogen vibrational energy due to the surrounding GaN.[4]

Emission spectra from samples *D* (nanocrystalline) and *E* (amorphous) are shown in Fig. 2(b), both recorded using $E_{ex}=399$ eV, which is above the GaN absorption edge but below the N_2 π^* resonance. The spectra have been normalized to their peak intensity at 394 eV. Although the low energy portion of both spectra are very similar, the high energy edge is steeper in the amorphous sample, and the valence band maximum thus lies at a lower energy by about 0.5 eV. This is consistent with an increased optical band gap measured in this and other amorphous samples,[3,5] most likely related to their high oxygen content. A similar comparison between spectra taken with E_{ex} far above the absorption edge will be the subject of a future study.

To conclude, the density of states of disordered GaN films shows increasing departure from that of crystalline GaN as the films go from nanocrystalline to fully amorphous. Features related to specific defects and impurities appear most noticeably close to the band edges. The results highlight the importance of the short-ranged structural properties in determining the electronic structure of disordered GaN, and demonstrate the effectiveness of x-ray absorption and emission spectroscopy for studying such effects.

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