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Optical studies of the effect of oxidation on GaN

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Optical studies are reported of GaN following oxide layer growth using thermal oxidation and atomic layer deposition (ALD). The low-temperature photoluminescence (PL) probes the topmost GaN layer (<100 nm) where any influence from the oxide is expected. Thermal oxidation results in a 6 meV blue shift of the main PL band (3.478 eV) that is attributed to stress due to formation of GaON/β-Ga_2O_3 upon the GaN surface. A weak PL feature at ~3.38 eV is due to diffusion of oxygen into the GaN. The Al_2O_3 deposited by ALD does not result in the 3.38 eV band following deposition and subsequent annealing. In contrast, HfO_2 deposited by ALD results in sub-band gap features, which strengthen upon annealing. No appreciable stress is observed for either oxide deposited using ALD, which are not expected to produce GaON/β-Ga_2O_3 layer. © *2014 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4858467]

I. INTRODUCTION

Electronic devices based on GaN suffer from high gate and drain leakage current and current dispersion due to surface states.[1–3] Insulators are needed as gate dielectrics to reduce leakage current, while surface states can be modified by passivation to suppress current dispersion.[1,2,4] Recent work has focused on using high-k materials such as Al_2O_3, HfO_2, and Ga_2O_3 as passivation and gate dielectric layers permitting increased physical thickness of the oxide and to reduce high gate and drain leakage current and current dispersion.[3–6]

Despite this progress, problems remain in the development of isolation oxides for use in GaN technology. Chang *et al*. showed that the ALD process for HfO_2 for surface passivation of GaN results in an interfacial layer between the oxide and the semiconductor identified as GaON.[7] Later work by this same group reported an abrupt interface between the Al_2O_3 and the GaN, which remains atomically smooth even after 750 °C annealing under nitrogen ambient.[8] Coan *et al*. also observed interfacial layer for HfO_2 and abrupt interface for Al_2O_3, and calculated a larger interface dipole for HfO_2, which they attribute to the interfacial layer.[9] The significant difference between these two interface profiles for different dielectric materials may result from interactions between the oxide with GaN surface.

Given that GaON is forming at the interface between GaN and HfO_2, a differential analysis of thermal GaON formation and that formed in the ALD HfO_2 process can shed light on the interface nature. The effects of thermal oxidation of GaN have been previously investigated, and the oxide was determined to be monoclinic β-Ga_2O_3.[10–12] Lin *et al*. reported that GaN oxidized at 850 °C shows good interface quality because of more complete oxidation of GaN.[13] This process forms fewer traps at the oxide/GaN interface. They also investigated the influence of annealing and reported that high temperature annealing can improve the interface quality between oxide/GaN layer. However, annealing increases intrinsic defects to form acceptor and donor traps and antisite defects. Nakano *et al*. examined the effects of thermal oxidation on GaN.[14] They conclude that a β-Ga_2O_3 layer forms on the surface and a graded gallium-oxynitride (GaON) transition layer, i.e., a GaN/GaON/Ga_2O_3 stack.

We report here optical studies of the effects of oxidation on GaN aimed at exploring the extent to which an interface oxide is formed and diffusion of oxygen into the GaN. Low-temperature photoluminescence (PL) spectroscopy is used to investigate the presence of oxygen incorporation. We begin by examining the effects of thermal oxidation on the near-surface GaN and observe oxygen incorporation. We then consider layers of HfO_2 and Al_2O_3 deposited by low-temperature atomic layer deposition (ALD). Interestingly, the HfO_2 deposition and anneal process is seen to result in oxygen incorporation into the GaN, while the PL studies following the Al_2O_3 process show no evidence of oxygen present in the GaN.

II. EXPERIMENT

The starting material was unintentionally doped, (0001)-oriented GaN samples grown on sapphire substrates by

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hydride vapor phase epitaxy with thickness of ~5 μm, carrier concentration $<10^{18}$ cm^{-3}, and dislocation density $<1 \times 10^9$ cm^{-2}.[15] Samples were cleaned in aqueous HCl and rinsed in deionized water. One sample was retained as a reference with no further processing. A 3-nm thick HfO_2 film was grown by ALD using tetrakis(ethylmethylamino)hafnium and water at a chamber temperature of 200 °C. Similarly, a 3 nm thick Al_2O_3 film was grown using ALD with trimethylaluminum and water with a chamber temperature of 250 °C. One piece each of the HfO_2 and Al_2O_3 samples were annealed at a temperature of 700 °C for 1 min in N_2 gas. Thermal oxidation was done at 800 °C for 30 min in O_2 atmosphere. TEM measurements revealed the thickness of the oxidation layer to be 4–4.5 nm with some crystallinity, consistent with a mixture of β-Ga_2O_3 and GaON, as reported in the literature.[10–12,14]

All PL measurements were carried out with samples at 12 K. Emission was excited using 290 nm laser light, which is absorbed in top <100 nm of GaN. Spectra were dispersed by a grating monochromator and detected using a cooled photomultiplier. To check the effects of oxide removal, the thermal oxide was etched in 35% HCl for 20 min at room temperature to fully remove the oxide. The experimentally determined PL line widths (full width at half maximum) of the primary emission were in the range of 13–19 meV.

We carried out Raman measurements using visible and ultraviolet (UV) excitation. Below band gap visible excitation (514.5 nm) probes the full GaN layer, thereby corresponding to an average measurement and used to confirm the crystal quality of the GaN. In contrast, the UV Raman measurements, with wavelength 363.8 nm, probe the top <100 nm of the GaN,[16,17] i.e., near the surface/interface where the oxide is expected to produce any effect and comparable to the PL probe depth. All Raman measurements were done with the samples at room temperature.

III. RESULTS AND DISCUSSION

A. Thermal oxidation

Figure 1 shows low temperature PL spectra prior to oxidation, following growth of the thermal oxide, and after stripping the oxide layer using the HCl etch. For the GaN reference sample the primary PL emission is observed at 3.478 eV corresponding to shallow donor-bound emission close to the band gap energy.[18,19] Following oxidation, this band blue shifts 6 meV and broadens slightly. One plausible cause for the observed shift is the presence of low compressive stress [<0.15 GPa (Ref. 20)], presumably from the GaON/β-Ga_2O_3 stack. The interpretation of the stress-induced blue shift is supported by the PL data obtained following removal of the oxide (Fig. 1), which shows that the PL band red shifts back to the original position of the reference GaN. The observed broadening following the oxidation, on the other hand, remains after subsequent removal of the oxide. Similarly, doping of the near-surface region of the GaN may result in PL broadening accompanied by a blue shift due to the Burstein–Moss effect. However, our observation that the broadening remains while the peak position returns to the preoxidation energy is inconsistent with the expected Burstein-Moss behavior. We attribute the broadening to the presence of defects, such as interstitial oxygen introduced by the thermal oxidation process.

The inset to Fig. 1 shows below band gap emission for the same series of samples (intensity on a semilog scale). In the reference GaN we observe two bands corresponding to the first and second order longitudinal-optic (LO) phonon sidebands. The second sideband near 3.28 eV also exhibits a low-energy tail, which has been previously attributed to donor–acceptor transitions.[21,22] Oxidation produces a broad feature below the band gap at ~3.38 eV, and the phonon sidebands are no longer clearly present in the spectrum, as seen in the inset to Fig. 1. For the spectra shown, obtained under identical conditions, the below band gap band shifts from 3.390 ± 0.001 to 3.383 ± 0.001 eV when comparing GaN post-thermal oxidation and following HCl removal of the oxide stack. This shift is within experimental error of the 6 meV red shift observed for the primary PL band, described above, allowing us to conclude that the broad 3.38 eV feature shifts with the band gap related PL emission. The oxygen-related PL band in the oxygen-doped GaN (GaN:O) is otherwise not affected by the removal of the GaON/β-Ga_2O_3.

It is reasonable to attribute the broadened below band gap PL features to the presence of oxygen in GaN. The oxygen is expected to diffuse into the GaN during the thermal oxidation process. Using previously published diffusion coefficients (D) for oxygen in GaN[23] and the process time t, we estimate a diffusion length $L_D \sim 2\sqrt{Dt}$ of 270 nm. A peak near 3.40 eV has been previously reported in GaN annealed in an oxygen atmosphere.[21] This band was attributed to emission from a donor–acceptor pair related to the presence of oxygen.[24] The donor–acceptor interpretation was supported by the laser pump power dependence of the emission, which was seen to blue shift with greater laser intensity.[21] Figure 2 shows the excitation laser intensity dependence of the PL spectra for our sample following HCl removal of the thermal oxide. Spectra are normalized to the primary PL

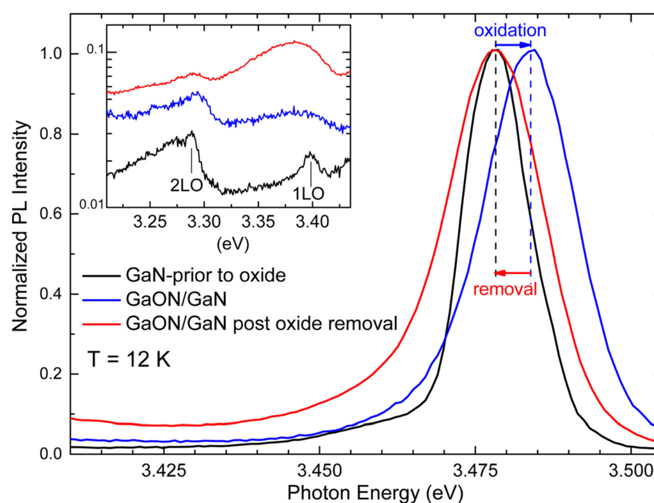

FIG. 1. (Color online) PL spectra of GaN as-grown, after thermal oxidization, and upon removal of the oxide. Spectra are normalized to the primary PL band shown. Inset shows below band gap emission on a semilog scale.

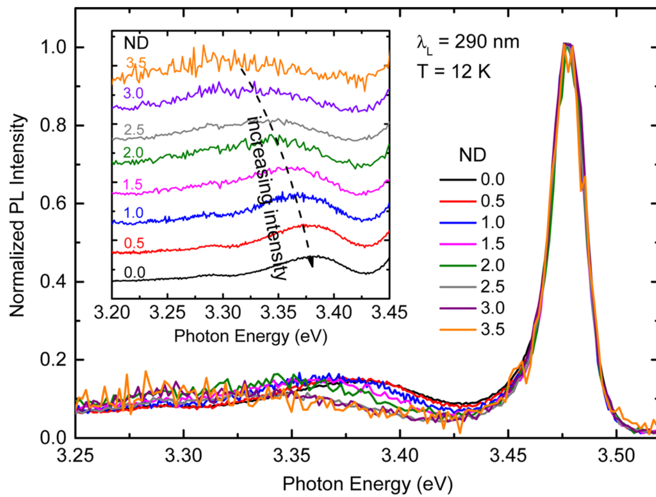

FIG. 2. (Color online) Power dependent PL spectra at 12 K of GaN upon removal of the oxide. Neutral density factor ND is used to obtain excitation intensity $I = 10^{-ND} I_0$.

emission intensity. Also shown, and with more detail in the inset to Fig. 2, is the ~3.38 eV band for this sample. This series of spectra has been rescaled so that the intensities are comparable. The data show this peak to blue shift with increasing laser power at a rate of ~20 meV per decade. Since the main PL peak neither shifts nor broadens across the same laser pump power range in Fig. 2, the shift observed in the 3.38 eV band is not due to changes in the band gap. We therefore attribute this PL emission to the oxygen-related donor–acceptor pair transition. The observation that this band remains following the HCl etch confirms that thermal oxidation produces a GaN:O layer, which is not removed by the HCl.

Our UV Raman measurements, obtained at room temperature and presented in Fig. 3, show the expected E_2^2 and A_1(LO) symmetry phonons superimposed on the band gap related PL emission. The intensities are normalized to the underlying PL. We see that the intensities of the E_2^2 and A_1(LO) bands are comparable in each spectrum. The latter band is intense due to near resonance conditions of the 363.8-nm (3.408-eV) excitation with the GaN energy gap at room temperature.[19] Prior studies of heavily oxygen doped GaN (~10^{19} cm^{-3}) revealed a band at 544 cm^{-1}, which was attributed to an oxygen vibrational mode.[25] Our results show no evidence of this band. Visible Raman measurements, not shown here, show similarly that the E_2^2 and A_1(LO) phonons do not shift between the different samples. This is as expected, since these measurements are sensitive to the full thickness of the GaN material, and therefore provide a average property throughout the layer. We conclude from this that the oxygen concentration in our samples is much lower than this value and that the PL measurement is more sensitive to low-level oxygen incorporation in GaN.

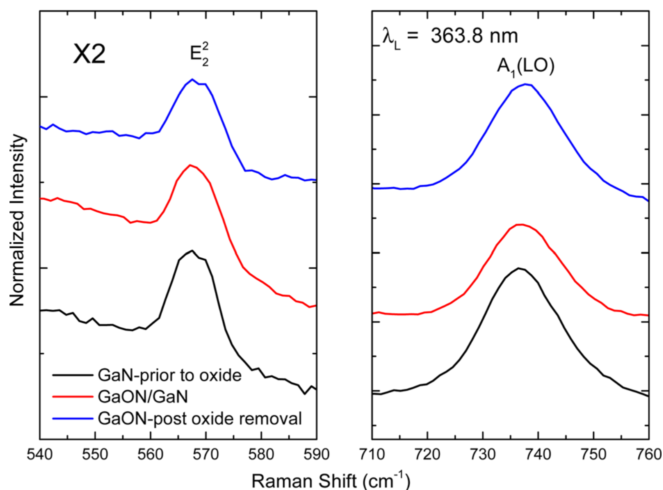

FIG. 3. (Color online) Room-temperature UV Raman spectra of GaN: as-grown, after thermal oxidization, and upon removal of the oxide. Spectra have been normalized to the background PL intensity and offset for clarity. The E_2^2 range has been scaled by a factor of two for clarity.

B. ALD oxides

Figure 4 shows PL data for the same reference sample, and for that same material following deposition of HfO_2 and Al_2O_3 (as deposited and following anneal). Very small shifts (<2 meV) are observed postdeposition, consistent with low stress levels introduced by these oxides, although we do see broadening of the GaN PL band. To check for oxygen incorporation, we measured the range below the band gap emission, inset to Fig. 4. For the sample with Al_2O_3, both pre- and postanneal, we see no substantial change in the PL, indicating that any oxygen incorporation in the GaN due to these processes remains low in concentration when compared with the high-temperature thermal oxidation step. In contrast, the HfO_2 deposition results in more intense below-band gap PL. This is seen in the emission at ~3.28 eV prior to annealing. Following anneal of this sample the 3.28 eV emission remains and the 3.38 eV band also appears. Since HfO_2 deposited on silicon is known to decompose above 500 °C (Ref. 26) and the oxygen may readily diffuse into the underlying GaN, it is reasonable to assume this also takes place in our samples. Estimating the oxygen diffusion length in GaN

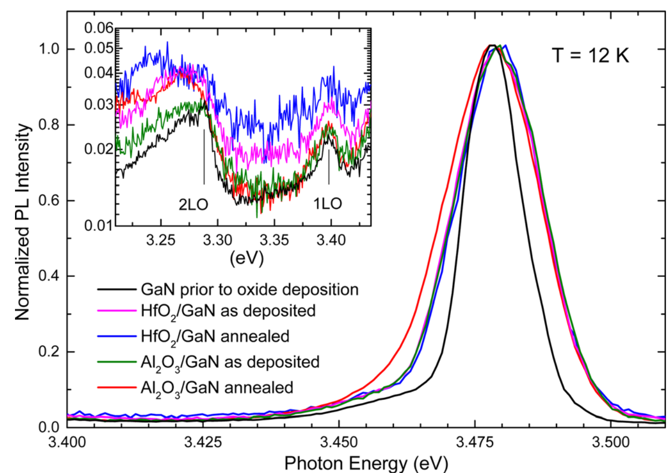

FIG. 4. (Color online) PL spectra of GaN as-grown and HfO_2 and Al_2O_3 film grown by ALD. Spectra are normalized to the primary PL band shown. Inset shows below band gap emission on a linear scale.

based on previously reported diffusion coefficients[23] and the post-ALD anneal conditions, we obtain $L_D \sim 40$ nm. Our results are consistent with the incorporation and activation of oxygen into the GaN following growth and postdeposition annealing of the HfO_2 layer.

IV. SUMMARY AND CONCLUSIONS

Our results show that low-temperature PL studies are useful for examining the effect of oxidation processing. Thermal oxidation results in formation of a GaON/β-Ga_2O_3 stack[14] and diffusion of oxygen into the GaN produces a band near 3.38 eV, which is attributed to oxygen present in the GaN. The GaON/β-Ga_2O_3 stack is removed by etching in aqueous HCl, but the GaN:O appears to be unaffected. For the processing conditions needed to obtain a 3 nm thick oxide, the diffusion length of oxygen into the GaN is approximately 270 nm. The UV light used to generate the PL and UV Raman scatter, with penetration depth $\sim$100 nm, is ideally suited to explore this region of the GaN. Deposition of HfO_2 using ALD, in contrast, appears to introduce oxygen into the GaN. This oxygen is present due to decomposition of the HfO_2 at elevated temperature[26] and activated by the same post-deposition anneal. The annealing conditions for the ALD oxides results in 40 nm diffusion length of oxygen in GaN, which is considerably smaller than the optical penetration depth of the UV excitation. The reduced relative intensity of the oxygen related PL band is attributable to the shallower diffusion region and possibly lower concentration. ALD of a thin Al_2O_3 layer on GaN does not appear to result in significant oxygen incorporation into the GaN. This may be the result of the high thermal stability of Al_2O_3.

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