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Interface Trap Density Reduction for Al_2O_3/GaN (0001) Interfaces by Oxidizing Surface Preparation prior to Atomic Layer Deposition

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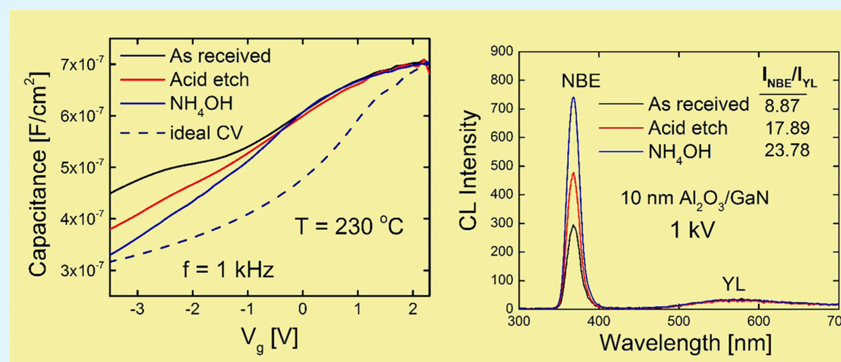

ABSTRACT: We correlate interfacial defect state densities with the chemical composition of the Al_2O_3/GaN interface in metal-oxide-semiconductor (MOS) structures using synchrotron photoelectron emission spectroscopy (PES), cathodoluminescence and high-temperature capacitance−voltage measurements. The influence of the wet chemical pretreatments involving (1) HCl +HF etching or (2) $NH_4OH_{(aq)}$ exposure prior to atomic layer deposition (ALD) of Al_2O_3 were investigated on *n*-type GaN (0001) substrates. Prior to ALD, PES analysis of the $NH_4OH_{(aq)}$ treated surface shows a greater Ga_2O_3 component compared to either HCl+HF treated or as-received surfaces. The lowest surface concentration of oxygen species is detected on the acid etched surface, whereas the NH_4OH treated sample reveals the lowest carbon surface concentration. Both surface pretreatments improve electrical characteristics of MOS capacitors compared to untreated samples by reducing the Al_2O_3/GaN interface state density. The lowest interfacial trap density at energies in the upper band gap is detected for samples pretreated with NH_4OH. These results are consistent with cathodoluminescence data indicating that the NH_4OH treated samples show the strongest band edge emission compared to as-received and acid etched samples. PES results indicate that the combination of reduced carbon contamination while maintaining a Ga_2O_3 interfacial layer by $NH_4OH_{(aq)}$ exposure prior to ALD results in fewer interface traps after Al_2O_3 deposition on the GaN substrate.

KEYWORDS: *GaN, atomic layer deposition, metal oxide semiconductor, interface trap density, surface treatments*

INTRODUCTION

The performance of conventional GaN-based high electron-mobility transistors (HEMTs) is limited by the excessively high leakage current of the Schottky gate.[1,2] High-κ materials are desirable for maintaining high gate capacitance and low gate leakage in dimensionally scaled transistors. For this reason, high-κ gate dielectrics have been investigated as a means of producing high performance field effect devices on GaN-based substrates for low static power consumption, improved transconductance and higher output power capabilities.[3−5] Amorphous aluminum oxide has become a popular candidate for the gate insulator by virtue of its large band gap ($E_g \sim 6.6$ eV),[6] dielectric constant ($\varepsilon \sim 8$),[7] breakdown field ($E_{[x]} \sim 10$ MV/cm)[8] and favorable band alignment with GaN.[9] In addition, Al_2O_3 has a very negative Gibbs free energy of formation (−1582 kJ/mol),[10] suggesting that it should exhibit good thermal stability during subsequent device fabrication. Studies of ALD of Al_2O_3 on GaAs[6] and InGaAs[11] have shown the existence of an ultrathin interfacial layer of defective native oxides on these semiconductor substrates as a result of their processing prior to ALD. However, reduction of these native oxides occurs during exposure to a trimethylaluminum (TMA) precursor used in Al_2O_3 deposition, indicating the potential to modify other III−V substrate surfaces by the ALD process alone.[12]

There have been several prior publications reporting the detrimental effects of surface/interface states on the performance of GaN-based devices, including threshold voltage (V_{th})-

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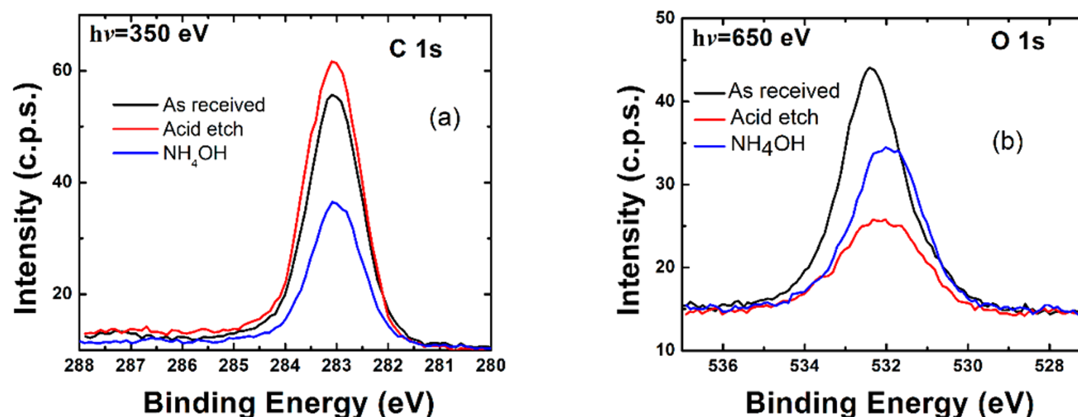

Figure 1. (a) Carbon 1s and (b) oxygen 1s core level spectra for various surface treatments taken at 350 and 650 eV electron energies, respectively, before Al_2O_3 deposition.

instability,[13,14] and current collapse due to charging of defects in the vicinity of the gate.[15] Methods to improve the device characteristics of GaN surfaces and interfaces have also been proposed.[9,16−19] They include surface cleaning procedures using aqueous $(NH_4)_2S$ and acid/base treatments involving species such as HCl, HF, NaOH and NH_4OH.[20,21] Wet chemical treatments are particularly attractive from a manufacturing perspective because of the ease of implementing wet etching steps in semiconductor processing. Surface oxide layers formed by wet chemical treatments can also serve as effective templates for initiation of atomic layer deposited dielectrics.[22] Therefore, understanding the relationship between GaN cleaning surface chemistry prior to atomic layer deposition (ALD) of high-κ gate dielectrics and the final metal-oxide-semiconductor (MOS) device electrical characteristics is very important.

To date, few studies correlate the chemical state of GaN surfaces with their interface trap densities in MOS devices.[23] In this report, the effectiveness of two promising surface preparations prior to ALD of Al_2O_3 on GaN is investigated in detail using synchrotron photoelectron emission spectroscopy (PES) analysis, cathodoluminescence (CL) and capacitance−voltage (C−V) measurements. Both surface cleaning methods result in Pd/Al_2O_3/n-GaN metal-oxide-semiconductor devices with interface electronic behaviors that are different from the case of an untreated surface. We find that aqueous $NH_4OH_{(aq)}$ pretreatment of as-received GaN (0001) reduces the interface trap density of the final MOS structures. This behavior is correlated with the presence of a gallium oxide surface layer onto which ALD of the Al_2O_3 dielectric takes place.

■ EXPERIMENTAL SECTION

Commercially obtained n-type GaN (0001) 2 in. diameter substrates grown by hydride vapor phase epitaxy were used for this work. The GaN was Si doped to an active concentration of $\sim 2 \times 10^{18}$ cm^{-3}. The surface of the GaN was cleaned using two different surface preparation procedures, (1) aqueous NH_4OH (15 min sonication in NH_4OH (pH ∼ 12); 5 min in deionized water; blow dried in N_2) and (2) the sequential combination of concentrated HCl and HF (pH ∼ 2.5).[19] A reference sample with no surface pretreatment (referred to as "as-received") was also included in the experiment matrix. In this study, ALD of Al_2O_3 was carried out in a load-locked reactor with 10^{-7} Torr base pressure by successive cycles of TMA and deionized water (DIW), with a precursor flow rate of 100 SCCM, TMA pulse time of 4 s and DIW 3 s, and a high purity N_2 purge time of 60 s was used between pulses. The substrate temperature was 270 °C, with a total pressure during ALD of $P \sim 0.2$ Torr. Two different thicknesses of ALD Al_2O_3 were deposited, ∼2 nm for PES and ∼10 nm for CL experiments and metal-oxide-semiconductor capacitor fabrication.

Synchrotron PES experiments were carried out at Beamline 10-1 of the Stanford Synchrotron Radiation Lightsource (SSRL), a wiggler source with a spherical grating monochromator covering a photon energy range from 250 to 1200 eV. The emitted photoelectrons were analyzed with a double pass cylindrical mirror analyzer with an approximate energy resolution of 0.25 eV. After chemical pretreatment, the samples were mounted to an Al sample holder using double sided carbon tape, and loaded into an ultrahigh vacuum chamber within 7 min (including ∼1 min of exposure to lab atmosphere). All the measurements were acquired in a single load, recording Ga 3d, N 1s, O 1s, C 1s and Al 2p core level regions at photon energies of 350, 650 and 950 eV. All of the XPS spectra were calibrated using the main C 1s peak, set to 285 eV, which was measured for all photon energies along with the other edges. The Cl 2p and F 1s regions were also scanned; however, no chlorine or fluorine was detected after either chemical pretreatment procedures or following dielectric deposition. Peak fitting of the resulting spectra was carried out using Analyzer peak fitting software,[24] utilizing fitting protocols described previously.[25]

Top-view CL measurements were performed at Lawrence Berkeley National Laboratory (LBNL) using a Zeiss Supra 55 VP-FESEM integrated with a custom built fiber-based CL system. The spectra were collected using an Acton spectrometer equipped with an AndorNewton[EM] camera and a Hamamatsu H7195 photomultiplier assembly. Noncontact mode atomic force microscopy (AFM) data from the as-received and post-treated GaN substrates were acquired using a Park Systems XE-70 scanning probe microscope with a scan rate of 0.5 Hz over 10 μm × 10 μm areas.

For metal-oxide-semiconductor (MOS) capacitor fabrication, the top metal contact consisted of 70 nm thick electron beam evaporated Pd deposited through a shadow mask. Blanket back metal contacts consisted of Ti of 20 nm thickness coated by 100 nm of Al, both by electron beam evaporation. C−V measurements were carried out in a shielded probe stations using a HP4284A precision LCR meter. The conductance method was used at elevated measurement temperature to estimate the interface density (D_{it}) on this MOS structure. At a high measurement temperature (230 °C), the interface trap response in the upper band gap (∼0.6 eV from the conduction band edge) can be probed using this technique.[26] In addition to interface traps, defects in the ALD-Al_2O_3 layer can trap electrons, as previously reported (see, for example, refs 27 and 28). To minimize their potential impact on D_{it} quantification, we were careful to restrict the range of applied bias to the depletion regime for these n-GaN substrates.

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RESULTS AND DISCUSSION

Figure 1a shows the C 1s spectra for as-received and chemically treated surfaces before Al_2O_3 deposition. Ammonium hydroxide exposure significantly decreases the surface concentration of carbon present relative to both the as-received and acid etched surfaces. We note that the acid etch slightly increases the detected carbon concentration on the surface.

Figure 1b shows the O 1s spectra for the described samples. Both chemical procedures are observed to cause a decrease in the surface concentration of oxygen present on the surfaces, particularly evident for the acid etched sample. The peak shift to a lower binding energy for the chemically treated surfaces relative to the as-received surface may result from removal of hydroxide related species in the surface adsorbate layer.[29] The carbon and oxygen surface coverages of the three samples after introduction to the UHV environment of the spectrometer (see Table 1) indicate that the $NH_4OH_{(aq)}$ treatment reduced the concentration of carbon by >45% and oxygen by >30%. In contrast, the HCl+HF etch resulted in a similar or slightly higher concentration of surface carbon and reduced the surface concentration of oxygen by >50% relative to that detected on the as-received sample. Considering the fact that chemically treated samples were exposed to air for a similar time (<1 min) prior to analysis, thus $NH_4OH_{(aq)}$ treatment is more effective at removing surface contaminants from the GaN wafer surface.

Table 1. Carbon and Oxygen Concentration in Surface Coverage % for Various Surface Treatments

element	as-received	acid etch	NH_4OH
C [%]	29.4	34.5	16.2
O [%]	12.5	6.7	8.9

To understand better substrate−gate oxide interface chemical bonding, Ga and N core level spectra were examined in more detail. Figure 2a shows Ga 3d spectra collected at 350 eV of photon energy for the chemically treated and as-received GaN surfaces before Al_2O_3 deposition. The spectra can be resolved into two components. The first one is ascribed to gallium bonded to nitrogen (bulk peak ∼20.2 eV). The second component (Ga_2O_3) is shifted toward higher binding energy by ∼0.8 eV and is ascribed to gallium bonded to oxygen, consistent with previously reported PES results.[30] There is no evidence of a Ga 1+ state; however, detection of this state is complicated due to the Ga−N peak having a similar binding energy to that of Ga_2O, as previously observed on GaAs and InGaAs samples.[31] As seen from Table 2, the HCl+HF etched sample reveals the smallest amount of Ga_2O_3 component with respect to bulk Ga, whereas the $NH_4OH_{(aq)}$ treated and as-received samples show similar amounts of Ga_2O_3. This result, combined with the C 1s data (Figure 1a), suggests that $NH_4OH_{(aq)}$ pretreatment results primarily in the reduction of surface carbon species, while maintaining a Ga_2O_3 surface layer prior to ALD.

Table 2. Ga_2O_3/GaN Ratio before and after Al_2O_3 Deposition

sample	Ga_2O_3/GaN ratio	
	before Al_2O_3	after Al_2O_3
as-received	0.21	0.18
HCl+HF etch	0.11	0.17
NH_4OH	0.23	0.16

The N 1s core level spectra for as-received and chemically treated samples before Al_2O_3 deposition are depicted in Figure 2b. All spectral features show a N−Ga peak at 397.3 eV and a N−GaO peak at ∼398.2 eV. Samples treated with NH_4OH also show a small, higher binding energy, feature at ∼400.5 eV assigned to a N−(CHO) peak (possibly consisting of O, C and H bonds).[32] However, this chemical state was not observed after thin Al_2O_3 deposition onto all three surfaces (not shown).

After ALD-Al_2O_3 film deposition, the amount of the Ga_2O_3 bonding component is similar for all three samples (Table 2). Atomic layer deposition using TMA, a potent reducing agent, as the Al precursor can lead to a "clean up" effect previously observed on various III−V substrates whereby pre-existing interfacial oxides are thinned down by reaction with TMA during the Al_2O_3 ALD process.[12,33,34] In contrast, dosing water vapor can oxidize III−V surfaces, even through a thin layer of already-deposited Al_2O_3.[35] The results summarized in Table 2 indicate that the effect of repeated TMA and H_2O exposure of the variously prepared GaN surfaces is to produce a similar amount of the Ga_2O_3 component at the interface after Al_2O_3 deposition across samples independent of their initial chemical state.[36] The interfacial Ga_2O_3 layer between Al_2O_3 and GaN

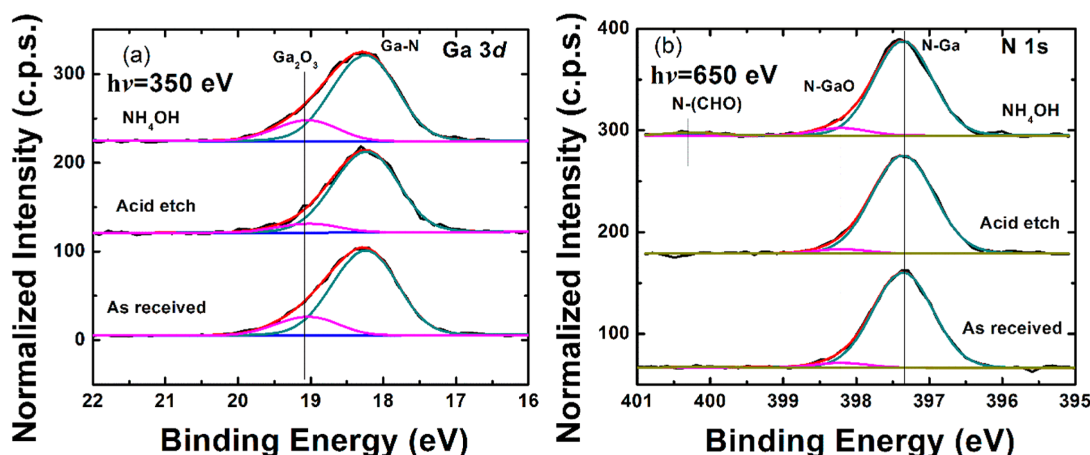

Figure 2. (a) Normalized gallium 3d and (b) nitrogen 1s core level spectra for various surface treatments taken at 350 and 650 eV incident photon energies, respectively.

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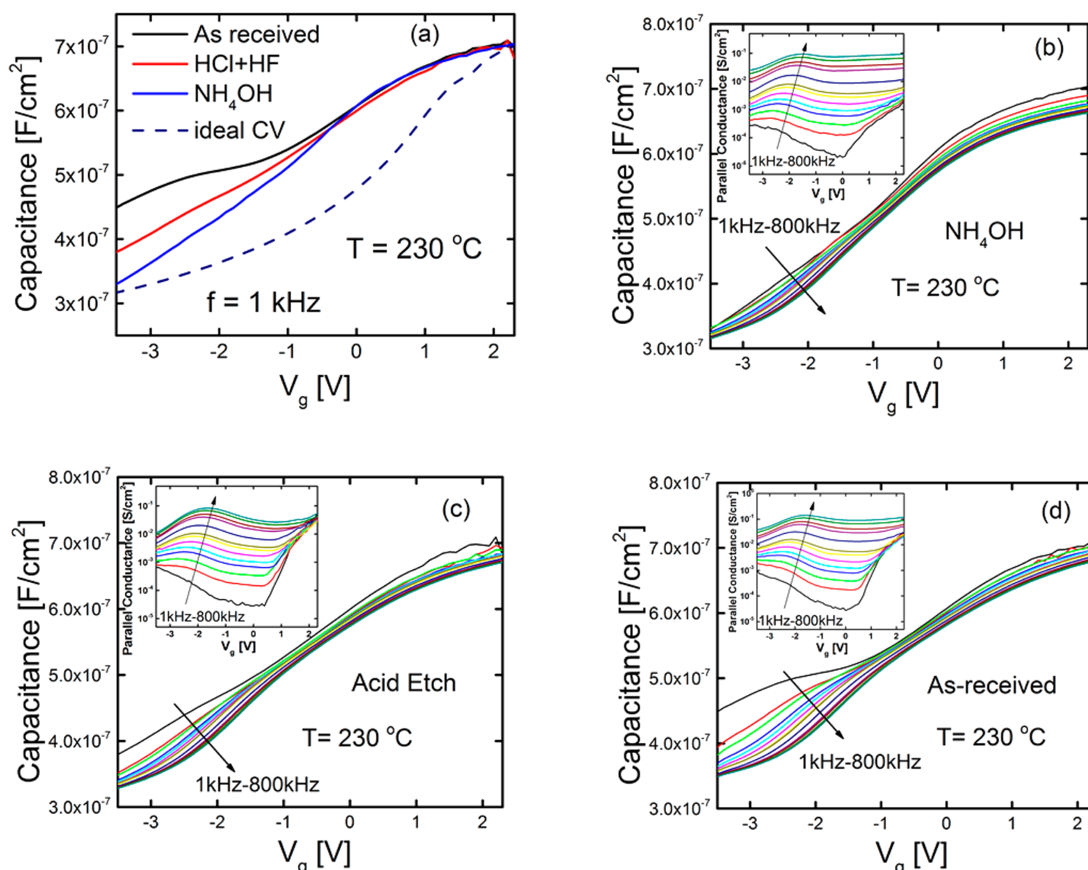

Figure 3. (a) $C-V$ characteristics of Pd/Al_2O_3/GaN MOS capacitors for various surface treatments measured at T = 230 °C, f = 1 kHz and ideal high frequency $C-V$ at room temperature, (b−d) $C-V$ characteristics as a function of frequency at 230 °C for pre-ALD surface treated in $NH_4OH_{(aq)}$, HCl+$HF_{(aq)}$ and as-received, respectively. The insets show their corresponding parallel conductance versus gate voltage.

substrate was not observed in cross sectional transmission electron microscopy images, perhaps because of limited contrast between amorphous ALD-Al_2O_3 and Ga_2O_3.[27] However, as will now be shown, the initial chemical state of the surface appears to affect the quality of the early stage Al_2O_3 growth and the resulting electrical characteristics of Al_2O_3/GaN MOS structures.

$C-V$ measurements have been routinely employed in the electrical evaluation of insulator−silicon interfaces.[26,27] As reported in refs 9, 26 and 27, in order to maximize the range of energies over which interface states can be measured in GaN-based MOS capacitors, high temperature $C-V$ measurements can bring the resonant frequency of traps located relatively deep in the band gap within the measurable ac frequency range of conventional semiconductor impedance analyzers. Figure 3a compares the $C-V$ characteristics of the pre-ALD surface treated and as-received GaN MOS capacitors measured at T = 230 °C, to the ideal high frequency $C-V$ curve at room temperature. The ideal high-frequency $C-V$ was simulated using the Van Dort analytical model to account for quantum mechanical effects.[37]

The distorted profile in the depletion region of the $C-V$ curve ($V_g < -1.5$ V) at 1 kHz indicates a higher interface state density for the as-received sample, with $D_{it} \sim 1.2 \times 10^{13}$ cm^{-2} eV^{-1} in the upper portion of the band gap (~0.6 eV from conduction band edge) extracted using the conductance method.[26,38]

Figure 3 shows the $C-V$ and $G-V$ characteristics as a function of frequency at 230 °C for the as-received, $NH_4OH_{(aq)}$-treated, and HCl+$HF_{(aq)}$-treated pre-ALD surfaces, respectively. As presented in Figure 3a, both of the wet cleans improve the final MOS $C-V$ characteristics compared to the as-received GaN. The removal of surface adsorbates and other trace impurities during the wet cleans may be responsible for this general reduction in dispersive, trap-related features. However, the sample treated with NH_4OH prior to ALD exhibits the smallest extracted (conductance method) interface trap density, with $D_{it} \sim 3.2 \times 10^{12}$ cm^{-2} eV^{-1} in the upper portion of the band gap. The ammonium hydroxide surface pretreatment is particularly effective in improving the electrical characteristics of the Al_2O_3/GaN MOS capacitors by reducing the density of interface states. According to the PES results, the improved interface quality after Al_2O_3 ALD compared to the acid clean appears to result from the combination of the presence of a stable Ga_2O_3 interfacial layer prior to ALD and the reduced carbon contamination after $NH_4OH_{(aq)}$ pretreatment.

Besides interface state density, surface roughness may influence the $C-V$ characteristics of MOS devices.[39] However, for the samples examined in the present study, there is no significant difference in the initial, pre-ALD, surface roughness values for the GaN substrate (see Table 3 and Figure 4). Moreover, the identical ALD process conditions used are not expected to lead to a difference in post-ALD Al_2O_3/GaN interface roughness.

$C-V$ analysis may not necessarily lead to a full understanding of the nature of such interface states, in part because this method is useful over relatively narrow energy ranges compared

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Table 3. RMS Values Extracted from AFM Measurements of 10 μm × 10 μm Sample Areas for Various GaN Surface Conditions

treatment	RMS roughness (in nm)
untreated	0.255
HCl+HF	0.251
NH_4OH	0.248

to the GaN bandgap of 3.4 eV.[9,26] Even when high temperature (500 K) capacitance−voltage measurements were used to maximize the observable defect density, clear defect responses in the measured conductance data were not always observed. Therefore, we investigated interface defects using a complementary and nondestructive technique, cathodoluminescence, that can provide an alternative insight into the energy states of these defects and their dependence on surface pretreatment prior to ALD of Al_2O_3 on GaN. The incident electron beam used in cathodoluminescence generates electron−hole pairs that induce electronic transitions with specific signatures of photon emission from deep levels and band edges.[40] The ability to tune the electron−hole generation depth by varying the accelerating voltage in CL measurement enables discrimination of the light emission signal from the bulk and near-interface regions of MOS structures.

Ten nanometers thickness of Al_2O_3 was deposited on bulk GaN (0001) substrates for the CL study. On the basis of simulation results obtained using the CASINO program[41] to predict the expected energy dependent electron interaction depths in this structure, an acceleration voltage of 1 kV was used to probe the interface region between the GaN and the 10 nm Al_2O_3 layer.[41] Figure 5 shows CL spectra of the pre-ALD surface cleaned and as-received Al_2O_3/GaN samples at room temperature. The CL spectra exhibit both deep-level yellow luminescence (YL) at a peak energy of 2.16 eV (574 nm) and near-band edge (NBE) emission at peak energies of 3.37 eV (368 nm) with peak intensity ratios of I_{NBE}/I_{YL} = 8.87, 17.89 and 23.78 for as-received, acid etched and $NH_4OH_{(aq)}$ treated samples, respectively. As illustrated in Figure 5, the peak intensity ratio of I_{NBE}/I_{YL} increases for GaN samples that underwent chemical surface treatment prior to ALD. Surface pretreatment using $NH_4OH_{(aq)}$ produced an especially large increase in the I_{NBE}/I_{YL}, indicating a reduction in the rate of nonradiative recombination at the Al_2O_3/GaN interface. Nonradiative recombination, typically the result of electronic states in the GaN band gap, is often caused by dangling bonds, adsorbed impurities, etc.[9,42] In agreement with the $C-V$ analysis, the $NH_4OH_{(aq)}$ cleaning procedure shows superior interface characteristics by CL. Considering the PES data

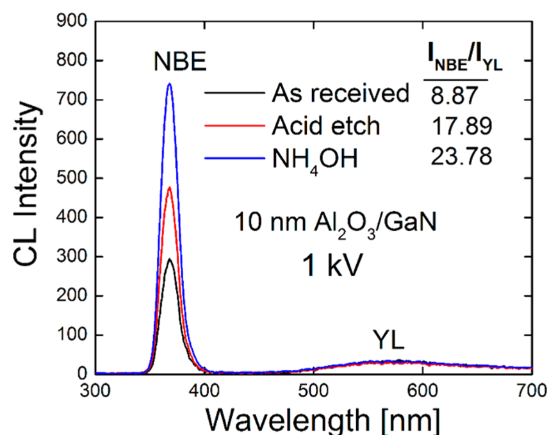

Figure 5. CL spectra and I_{NBE}/I_{YL} of 10 nm Al_2O_3/GaN for various surface treatments taken at acceleration energy (E) = 1 kV, and scan size = 114 μm × 114 μm at room temperature.

obtained from identically processed samples, a plausible explanation for this finding is that this cleaning method provides a lower surface carbon concentration while producing a Ga_2O_3-like surface layer. This cleaner oxide starting surface appears to produce a superior interface during the initial stages of ALD of the Al_2O_3 dielectric.

CONCLUSIONS

In summary, this study of surface treatment of GaN substrates prior to ALD of an Al_2O_3 gate dielectric yields the following findings: $NH_4OH_{(aq)}$ pretreatment results in greater Ga_2O_3 component at the interface, as detected by synchrotron PES analysis, compared to the HCl+HF treatment. The surface concentration of carbon contaminants detected on the chemically pretreated GaN (1000) surface is the lowest for the $NH_4OH_{(aq)}$ procedure. Both surface pretreatments improve electrical characteristics of the resultant metal-oxide-capacitors compared to MOS structures on as-received GaN substrates, as indicated by a lower measured interface state density. The lowest interface defect density was detected for samples treated with $NH_4OH_{(aq)}$ prior to Al_2O_3 ALD. This is consistent with CL data indicating that both surface pretreatments enhance the peak intensity ratio of I_{NBE}/I_{YL} by reducing the rate of defect-mediated nonradiative recombination of excited electrons and holes near the GaN surface, but that the $NH_4OH_{(aq)}$ treatment is more effective. These observations suggest that removing surface adsorbates and trace impurities by surface cleans, while maintaining a Ga_2O_3 interfacial layer using NH_4OH(aq) (which also reduces carbon contamination) produces fewer interface traps in ALD-Al_2O_3 gate stacks on GaN substrates.

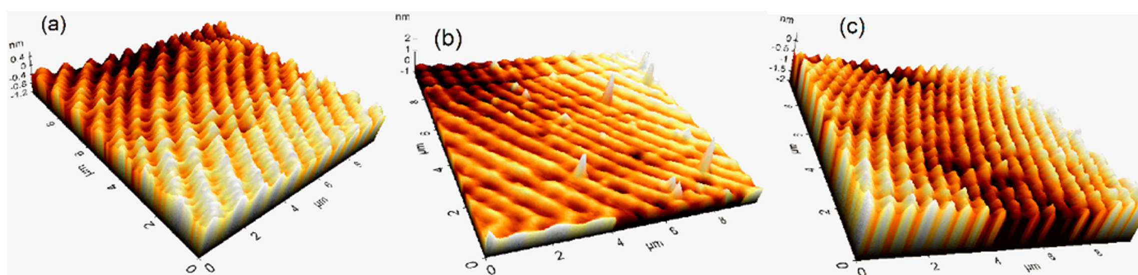

Figure 4. AFM images taken on 10 μm × 10 μm area of (a) as-received, (b) acid etch and (c) NH_4OH treated bulk GaN surface before Al_2O_3 deposition.

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Notes

The authors declare no competing financial interest.

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