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# Preparation of gallium nitride surfaces for atomic layer deposition of aluminum oxide

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A combined wet and dry cleaning process for GaN(0001) has been investigated with XPS and DFT-MD modeling to determine the molecular-level mechanisms for cleaning and the subsequent nucleation of gate oxide atomic layer deposition (ALD). *In situ* XPS studies show that for the wet sulfur treatment on GaN(0001), sulfur desorbs at room temperature in vacuum prior to gate oxide deposition. Angle resolved depth profiling XPS post-ALD deposition shows that the a-Al<sub>2</sub>O<sub>3</sub> gate oxide bonds directly to the GaN substrate leaving both the gallium surface atoms and the oxide interfacial atoms with XPS chemical shifts consistent with bulk-like charge. These results are in agreement with DFT calculations that predict the oxide/GaN(0001) interface will have bulk-like charges and a low density of band gap states. This passivation is consistent with the oxide restoring the surface gallium atoms to tetrahedral bonding by eliminating the gallium empty dangling bonds on bulk terminated GaN(0001). © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4894541]

#### I. INTRODUCTION

Gallium nitride (GaN) transistors support high power and high frequency operation. Typically, GaN transistors are depletion mode field-effect transistors that operate using Schottky gates, but high gate leakage and interest in creating enhancement mode transistors has prompted investigation into insulated gate structures.<sup>1,2</sup> Insulated gate device performance is highly sensitive to defects in the dielectric and at the insulator/semiconductor interface.<sup>3</sup> Without proper passivation, these defects can result in degradation of carrier mobility, anomalous time-dependence of device current, timedependent breakdown, decrease in transconductance, and pinning of the Fermi level.<sup>4</sup> Silicon nitride  $(Si_3N_4)$  is currently the standard for passivation of GaN surfaces because it readily forms an interface to GaN with good electrical properties.<sup>5,6</sup> Unfortunately, the band offset of silicon nitride on GaN is relatively small due to its modest band gap (5 eV), so the barrier to tunneling between the gate and channel is insufficient to significantly reduce leakage current when silicon nitride is used as a gate dielectric.

To reduce gate leakage, some groups have proposed alternative dielectrics such as  $Al_2O_3$ ,  $Ta_2O_5$ , and  $SiO_2$  which have larger band gaps.<sup>7–10</sup> For this study,  $Al_2O_3$  was chosen because it has a large conduction band offset with respect to GaN as well as a high permittivity (8-10) which allows for support of greater electric fields.<sup>9,11</sup> Unfortunately, deposition of  $Al_2O_3$  on air exposed GaN(0001) does not readily form a low-defect interface.<sup>11,12</sup> Cleaning and preparation of the surface prior to oxide deposition is required to passivate interfacial defect states.<sup>11–13</sup> Studies have demonstrated success in removing the native oxide on GaN using various wet cleaning procedures.<sup>14,15</sup> Additionally, there have been reports of improvement in oxide quality on GaN after exposure to trimethylaluminum (TMA) and atomic hydrogen prior to atomic layer deposition (ALD).<sup>16</sup> This effect is well documented on other III-V materials, as well.<sup>17–20</sup> In this study, both *ex situ* wet cleans and *in situ* dry cleaning combinations were investigated to better understand the underlying atomic-level interactions at play.

Density functional theory (DFT) was used to predict the most stable state for several configurations of oxide-GaN(0001) interfaces as well as to illustrate the defect sites responsible for any interfacial trap states. To verify these models, an *ex situ* wet clean using sulfur and *in situ* dry cleaning with TMA and atomic hydrogen were performed, and the resulting interfaces characterized via XPS and capacitancevoltage profiling.

#### **II. EXPERIMENTAL AND MODELING DETAILS**

#### A. DFT-MD modeling

To model both an ideal defect-free interface as well as the experimental interface, this study employed DFT with molecular dynamics (MD). Simulations were performed with the Vienna *Ab Initio* Simulation Package (VASP) using projector augmented-wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhor (PBE) exchange correlation functional.<sup>21–25</sup> The amorphous Al<sub>2</sub>O<sub>3</sub> model was generated in accordance

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with the method detailed by Chagarov and Kummel.<sup>26</sup> In the generation of the amorphous  $Al_2O_3$  samples, crystallization was never observed even for annealing at 5000 K consistent with amorphous  $Al_2O_3$  being very stable. After initial stacking of the a- $Al_2O_3/GaN$  systems, they were partially relaxed for ~30 conjugate-gradient (CG) relaxation steps, annealed at 800 K for 1000 fs with 1.0 fs timesteps, cooled to 0 K for 200 fs, and finally relaxed below a 0.05 eV/Å force tolerance level. Three bottom layers of the GaN slab were permanently fixed in their bulk-like positions. Since the standard DFT PBE exchange-correlation functional underestimates the GaN band gap value, the PBE-relaxed systems were rescaled from PBE to HSE06 GaN lattice constant value and more accurate HSE06 hybrid-functional electronic structure was calculated.<sup>27–29</sup>

#### B. Cleaning study

Both *ex situ* wet cleaning and *in situ* dry cleaning methods were investigated to determine the effects on surface contamination and ALD nucleation density. Three sets of experiments were performed: X-ray photoelectron spectroscopy (XPS) of the surface after wet cleaning, XPS of the early stages of ALD deposition, and capacitance-voltage measurements of samples with a thicker oxide. For the first experiment, samples were exposed only to the wet clean process, and their surfaces probed with XPS for the presence of contamination or native oxide reformation. The second and third experiments included the addition of an *in situ* dry cleaning process to the *ex situ* wet cleaning.

All samples in this study were GaN(0001) grown via MOCVD on sapphire substrates, and for each of the three experiments every sample first received an *ex situ* wet clean treatment. For step one of this wet treatment, all samples were first given an organic clean consisting of sequential dips in acetone, methanol, isopropanol, and deionized water. For step two, all samples received a dip in 6%HCl<sub>(aq)</sub> for 1 min at room temperature. For step three, all samples were dipped in a 7%NH<sub>4</sub>OH<sub>(aq)</sub> solution for 1 min at room temperature. As shown by Hattori et al., the acid and base treatments ensured that the native oxide present on the air-exposed samples was removed.<sup>15</sup> After step three, two different treatments were tested with one group receiving a final dip in 5%  $(NH_4)_2S_{(aq)}$ for 30 min at 50 °C and the other group bypassing this treatment. The sulfur treatment is expected to prevent reoxidation in ambient during transfer to the vacuum ALD system consistent with experiments on InGaAs<sup>30,31</sup> and GaAs.<sup>32</sup> After each step, samples were rinsed in deionized water for 1 min and then dried in N<sub>2</sub> gas.

For the first experiment, the effect of each individual step of the *ex situ* wet clean was documented using *in situ* monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Nanotechnology). Following each clean, samples were immediately loaded into ultra-high vacuum at a base pressure of  $2 \times 10^{-10}$  Torr. XPS measurements were taken at room temperature without any prior thermal annealing. Following this set of experiments, samples which had the complete wet clean process were annealed in UHV at 50 °C increments ranging from 150 °C–450 °C. The ramp rate for each thermal anneal

TABLE I. Summary of ALD pretreatments.

| Pretreatment | $(NH_4)_2S$ wet clean | TMA only | TMA and atomic hydrogen |
|--------------|-----------------------|----------|-------------------------|
| A            | No                    | Yes      | No                      |
| В            | Yes                   | Yes      | No                      |
| С            | No                    | No       | Yes                     |
| D            | Yes                   | No       | Yes                     |

was 1 °C/min. At each 50 °C step, *in situ* XPS spectra were collected. For all measurements, the XPS was operated in constant analyzer energy mode with a pass energy of 50 eV and beam width of 0.1 eV using an Al K $\alpha$  source. A detector angle of 30° with an acceptance of  $\pm$ 7° was used to maximize surface sensitivity. The spectrum analysis was performed using CASAXPS v2.3. The relative XPS intensity of each core peak (Ga, N, O, C, S) was obtained using Shirley fitting and dividing the calculated area under each peak by its Scofield XPS sensitivity factor.

For the second group of experiments investigating the early stages of ALD deposition, the samples were first treated using the wet organic, acid, base, and sulfur clean processes described above. The two groups of samples (with/without  $(NH_4)_2S$  dip) were further divided based on two types of in situ dry cleaning: those which received 5 cycles of TMA and those which received 5 cycles of atomic hydrogen/TMA/atomic hydrogen prior to the start of deposition which is identical to the in situ H/TMA/H method reported by Son et al.<sup>33</sup> In total, this produced four distinct combinations of wet and dry ALD pretreatments which have been denoted by letters A-D. A summary of these treatments is shown in Table I. The in situ treatments were performed in the ALD chamber (Oxford Instruments FlexAl ALD) at a temperature of 300 °C. For the pretreatments, each TMA cycle consisted of a 40 ms pulse at a pressure of 200 mTorr with Ar carrier gas flow of 100 sccm followed by a 5 s Ar purge, and finally a H<sub>2</sub> gas stabilization step for 10 s.<sup>34,33</sup> Each atomic hydrogen pulse was generated using an Oxford FlexAl plasma source with an ICP forward power of 100 W and consisted of exposure to the plasma for 2 s at a H<sub>2</sub> pressure of 20 mTorr.

Immediately following completion of each pretreatment, all samples received 8 cycles of ALD to deposit  $Al_2O_3$  on the surface at 300 °C using TMA as the metal precursor and water as the oxidant. The TMA half-cycle consisted of a 500 ms TMA pulse at 20 mTorr with an Ar carrier gas flow of 100 sccm and a 7 s Ar purge at 200 mTorr. Each oxidant half-cycle consisted of a 500 ms water pulse at a pressure of 200 mTorr with an Ar carrier gas flow of 250 sccm which was followed by a 7 s Ar purge at 200 mTorr. Between each halfcycle, the chamber was evacuated for 7 s and subsequently flushed with Ar for 7 s at 200 mTorr.

To examine the state of interfacial bonding, Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) measurements were obtained using an XPS VG Theta Probe system with an Al K $\alpha$  (1486.7 eV) excitation. Samples were placed on the holder using Cu-Be pins as a support, pumped down in the load lock, and subsequently transferred into the chamber at a pressure of 3  $\times$  10<sup>-9</sup> Torr. Angle resolved

spectra were obtained in the range of  $26.75^{\circ}-79.25^{\circ}$  with a step size of  $7.5^{\circ}$ . The system was operated with a pass energy of 150 eV. A 9.5 eV flood gun was employed to compensate for the charging of samples. The theta-probe ARXPS measurements were made *ex situ* to determine the bonding at the buried interface. No post-deposition annealing was performed after the samples were exposed to ambient to ensure an unchanged interface. This 25 °C air exposure is identical to the exposure on the sample used for capacitance-voltage (C-V) measurements and, therefore, reflects the most realistic interface.

For the final experiment, C-V measurements were performed using an Agilent B1500 Semiconductor Analyzer on samples which had the same four pretreatments A-D. In this case, however, a thicker oxide was required so the number of ALD cycles was increased from 8 to 80. The ALD process parameters are identical to those described above. The details of the (C-V) measurements have been outlined in a separate study.

#### **III. RESULTS AND DISCUSSION**

#### A. DFT modeling

Most GaN transistors have n-type channels since they are typically used in power devices, so defect states near the conduction band edge or mid-gap position are of the greatest concern. Therefore, a successful pre-ALD cleaning procedure for GaN devices would need to passivate the defects responsible for these trap states. To identify the source of problematic interface states in the amorphous Al<sub>2</sub>O<sub>3</sub>/GaN system, DFT calculations were performed to obtain the density of states and band-decomposed charge density fields for the bulk-terminated surface, a-Al<sub>2</sub>O<sub>3</sub> bonded to a layer of crystalline Ga<sub>2</sub>O<sub>3</sub>,<sup>35</sup> and a-Al<sub>2</sub>O<sub>3</sub> bonded directly to the Gapolar GaN(0001) surface. The final state of each system was determined using DFT-MD annealing, cooling, and final relaxation. This allowed for the analysis of an amorphous oxide layer at finite temperature as it relaxed to its most stable state.

Feenstra prepared a nearly ideal oxide/GaN stack by in situ thermal oxidation of the gallium ad-layer on GaN(0001) MBE grown samples. Both scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) showed the surface oxide layer to be crystalline, and scanning tunneling spectroscopy (STS) showed the surface Fermi level to be unpinned.<sup>35</sup> The experimental unit cell is too large to be modeled using a full oxide stack, so a simplified model was employed substituting an O-Ga-O layer with approximately the same structure as GaN. On top of the crystalline O-Ga-O layer, amorphous oxide was bonded and annealed at 800 K for 1000 fs with 1.0 fs time steps, cooled to 0 K for 200 fs, and finally relaxed below 0.05 eV/Å force tolerance-level using DFT-MD. The total system consists of 174 atoms. The O-Ga-O layer never became disordered since these DFT-MD simulations were limited to 800 K which is still well above oxide ALD growth temperatures. The annealed/relaxed structure is shown in Fig. 1(a) along with the corresponding density of states (DOS) (Fig. 1(b)). The model shows the interface is not quite ideal since there are a few undercoordinated atoms at the a-Al<sub>2</sub>O<sub>3</sub>/O-Ga-O interface and within the O-Ga-O layer. The undercoordinated oxygen atom is denoted by a blue arrow while the undercoordinated gallium atom is denoted by a red arrow. The gallium and oxygen dangling bonds normally produce states within the bulk band gap, but since these undercoordinated atoms are in a wide band gap oxide layer they may not produce states inside the band gap of the full a-Al<sub>2</sub>O<sub>3</sub>/O-Ga-O/GaN stack. This is a crucial point when considering the operation of MOSFETs on GaN(0001). Off-state performance of n-type devices on GaN(0001) is not significantly impacted by states inside the valence band due to the large semiconductor band gap, so those defects can be safely disregarded. States outside the GaN band gap, but near the band minimum, could degrade MOSFET performance, but in this case they are of a relatively low density. The low density of defect states inside the conduction band could necessitate a slightly higher gate voltage, but this is not critical for power devices in contrast to logic devices. Therefore, due to the presence of the ordered O-Ga-O layer, the defect states predicted to form in this system will have minimal effect on device performance.

The HSE DOS shows that the annealed structure has only two small mid-gap states, which are indicated in Fig. 1(b) as A and B. To determine whether either of these states were the result of the two undercoordinated atoms present in the model, the band decomposed charge densities were calculated for states A and B. The results of these calculations are shown in Figs. 1(c) and 1(d) with regions of highest charge density highlighted in purple. The band decomposed charge density for conduction band state A (Fig. 1(c)) is delocalized across oxygen atoms in the crystalline O-Ga-O layer. There is not significant charge concentration on the undercoordinated atoms indicating that this state is not caused by aberrant interfacial bonding. The band decomposed charge density for the final state, B, is centered on atoms at the vacuum/a-Al<sub>2</sub>O<sub>3</sub> interface. This state arises due to limitations of the DFT vacuum/oxide passivation technique and is therefore inconsequential. Overall, the band decomposed charge density breakdowns show no mid-gap states resulting from aberrant bonding at any interface. This is consistent with defects in the O-Ga-O layer producing states outside the GaN band gap.

To understand how the O-Ga-O layer is able to passivate the interface, a Bader charge analysis was performed. Gallium atoms from the O-Ga-O layer have -0.32 (from -0.36 to -0.29) lower Bader charge values (more positive) than those in bulk GaN. These results suggest that Ga atoms in the O-Ga-O layer have charge similar to Ga in bulk GaN. Because the gallium in the O-Ga-O layer is bulk-like, these bonds produce states very similar to bulk GaN therefore resulting in a clean band gap.

While the crystalline  $Ga_2O_3$  interlayer may form a nearly ideal interface when grown via *in situ* thermal oxidation, producing this structure repeatedly and reliably is challenging on a larger scale. Additionally, maintaining the state of the  $Ga_2O_3$  interlayer can present issues during subsequent device processing like the ALD deposition due to the relatively low thermal stability of  $Ga_2O_3$ . While a-Al<sub>2</sub>O<sub>3</sub>/O-Ga-O/GaN



FIG. 1.  $a-Al_2O_3$ /ordered O-Ga-O interlayer/GaN(0001). (a) DFT model of annealed and relaxed amorphous  $Al_2O_3$  on an ordered O-Ga-O interlayer on GaN(0001) surface. Undercoordinated oxygen and gallium atoms are denoted by blue and red arrows, respectively. (b) The HSE density of states for the  $a-Al_2O_3/O$ -Ga-O/GaN(0001), O-Ga-O/GaN(0001) without  $Al_2O_3$  passivation, and GaN bulk systems. The edges of the bulk GaN band gap are indicated by the blue and purple vertical lines at approximately -3.5 eV and -0.2 eV. (c) The decomposed charge density for state A. The conduction band edge state, A, is on the N atoms near the O-Ga-O/GaN interface as well as oxygen atoms within the O-Ga-O layer. The undercoordinated oxygen and gallium atoms in the ordered O-Ga-O layer do not contribute to the A state. (d) The decomposed charge density for state B. The conduction band edge state, B, is mostly at the vacuum/ $Al_2O_3$  interface and is therefore not important.

structure can be prepared experimentally, in this study the DFT model of a-Al<sub>2</sub>O<sub>3</sub>/O-Ga-O/GaN was employed for comparison to the a-Al<sub>2</sub>O<sub>3</sub>/GaN structure to determine the role of weakly bound electrons in dangling bonds at the oxide interface. To investigate a more practical structure the case of a- $Al_2O_3$  directly bonded to the GaN(0001) surface has also been modeled. These models are shown in Fig. 2. As indicated by the arrows in Fig. 2(a), the annealed a-Al<sub>2</sub>O<sub>3</sub>/GaN(0001) simulation has three defective sites-a Ga atom with a dangling bond (red arrow) and two Ga-Al metal-metal bonds (blue arrows). While the dangling bonds in the O-Ga-O layer in Fig. 1 are in a wide band gap oxide, the dangling bond and metallic bonds in Fig. 2 system are located directly on the semiconductor. Unlike those in the wide band gap oxide, the aberrant bonds in this case are expected to create states in the band gap.

Fig. 2(b) compares the DOS for the a-Al<sub>2</sub>O<sub>3</sub>/GaN(0001) stack with that of the bulk GaN and clean unpassivated bulk terminated GaN(0001). The DOS shows that while the a-Al<sub>2</sub>O<sub>3</sub>/GaN(0001) passivated many of the mid-gap states of clean GaN(0001), there are band gap states on a-Al<sub>2</sub>O<sub>3</sub>/GaN(0001) which are not present in bulk GaN(0001).

To determine if the band gap states of  $a-Al_2O_3/GaN(0001)$  originate at interfacial defects, band-decomposed charge densities were calculated for the three states denoted by arrows in Fig. 2(b). Band-decomposed charge simulations show that the two Ga-Al metal-metal bonds (blue arrows) are responsible for the valence band edge states A, while the gallium dangling bond is the origin of the conduction band edge states B and C. The results are consistent with the need to passivate all dangling bonds and remove all metallic bonds which are directly on the GaN(0001) surface.

To understand how the  $Al_2O_3$  passivates the GaN(0001) (except for the metallic and dangling bonds), a Bader charge analysis was performed comparing interfacial atoms to their respective bulk counterparts. Bader charge calculations for a- $Al_2O_3/GaN(0001)$  indicated interfacial aluminum atoms have nearly bulk-like bonding as interfacial aluminum atoms have only +0.02 |e| (from 0.0 to +0.03) higher Bader charges (more negative) than those in bulk a- $Al_2O_3$ . Along the same lines, interfacial oxygen atoms have -0.12 |e| (from -0.08to -0.18) lower Bader charges (more positive) than oxygen atoms in bulk a- $Al_2O_3$ . The interfacial gallium atoms (except the two Ga's bonded to Al) have deviations of only -0.01 |e|



FIG. 2.  $a-Al_2O_3/GaN(0001)$ . (a) Model of amorphous  $a-Al_2O_3$  bonded directly to Ga-polar GaN(0001). The blue arrows highlight two metallic Ga-Al bonds and a red arrow highlights an undercoordinated Ga atom. (b) The HSE density of states for  $a-Al_2O_3/GaN(0001)$ , unpassivated GaN(0001), and bulk GaN. The arrows designate states A and B which exist within the bulk band gap (which is shown via blue and purple vertical lines for clarity). The  $a-Al_2O_3$  has passivated most of the surface states on the clean Ga-polar GaN(0001) surface. (c) The band decomposed charge densities of valence band edge state A. The states are concentrated on the Ga-Al metallic bonds (blue arrow in Fig. 2(a)). (d) The band-decomposed charge densities of conduction band edge state B, which originates on an undercoordinated Ga atom (red arrow in Fig. 2(a)). (e) The band-decomposed charge density of state C in the conduction band, which is caused by the presence of undercoordinated Ga atoms (red arrow in Fig. 2(a)).

(-0.11 to +0.22) compared to gallium in bulk GaN. However, the two gallium atoms belonging to the Ga-Al bonds have Bader charge deviations of +0.94 and +0.96 (more negative), and the gallium atom not forming a bond to the oxide has a Bader charge deviation of +0.22 (more negative). This shows that for the conduction band edge states on the gallium atom with a dangling bond, a state forms in the band gap due to the weak binding of electrons in the dangling bond instead of aberrant charge. The presence of strong, ionic Ga-O bonds in the a-Al<sub>2</sub>O<sub>3</sub>/O-Ga-O/GaN(0001) model shifts gallium dangling bond states to energies outside the band gap while in the case of  $a-Al_2O_3$  directly bonded to GaN(0001), the covalent bonding to the GaN bulk creates dangling bonds with states that exist within the bulk band gap. Despite the formation of these sites, the Al<sub>2</sub>O<sub>3</sub> still passivates most states and results in a relatively clean band gap. The interfacial dipoles were calculated for both the  $Al_2O_3/GaN(0001)$  and  $Al_2O_3$  $/GaN(000\bar{1})$  interfaces and found to be of similar magnitude of opposite sign (17.17 vs  $-18.08 |e| \times Å$ ) consistent with at least partial passivation of the polarization bound charge. As a comparison, included in the supplementary material<sup>43</sup> are DFT-MD results describing Al2O3 passivation of the N-polar  $GaN(000\overline{1})$  which demonstrate how the polarization charge is compensated by the oxide. To obtain complete passivation, ALD will need to be nucleated in every unit cell to insure all dangling bonds are eliminated.

#### B. Cleaning study

To understand the mechanisms of contamination removal and gallium dangling bond passivation, a two-part cleaning process was employed consiting of an *ex situ* wet clean and an *in situ* dry clean performed immediately prior to ALD of  $Al_2O_3$ . The first portion of the study examined the wet clean alone to determine its effect on the state of the surface. The XPS data shown in Fig. 3(a) compare the oxygen and carbon coverage on the GaN(0001) surface for samples having received one of three *ex situ* wet cleans while the XPS data in Fig. 3(b) examine those coverages for samples which have been cleaned using HCl, NH<sub>4</sub>OH, and (NH<sub>4</sub>)<sub>2</sub>S and annealed in UHV. The coverages of oxygen and carbon have been normalized to the total gallium signal. The control samples, which received only the organic solvent degrease, served to establish a baseline for the initial condition of the surface.

The unannealed organic solvent cleaned samples show a 50% oxygen and 100% carbon coverage (normalized to Ga) (Fig. 3(a)). For the samples cleaned using the 6%HCl and 7%NH<sub>4</sub>OH solutions, the coverage of surface contaminents





FIG. 3. In situ XPS study of the effects of wet cleaning and annealing on GaN(0001). Carbon and oxygen coverage for (a) samples wet cleaned in HCl,  $NH_4OH$ , and  $(NH_4)_2S$  without *in situ* anneal and (b) UHV annealing performed from 150–450 °C. Without annealing, the addition of the HCl and  $NH_4OH$  cleans reduced the carbon and oxygen contamination to 40% and 25%, respectively. The  $(NH_4)_2S$  treatment reduced the oxygen coverage to approximately 10% but had only a small effect on surface carbon. The UHV annealing experiments indicated that the majority of residual oxide desorbed above 200 °C but the carbon was not completely removed. The variation in oxygen and carbon is likely due to the measurements being taken over several days and limited XPS sensitivity. The error bars reflect the range of values obtained from multiple fittings of the XPS spectra.

was reduced to approximately 30% oxyegn and 50% carbon. For the samples which also received the  $5\%(NH_4)_2S(aq)$  treatment, the amount of oxygen and carbon on the surface was further reduced to 10% oxygen and 30% carbon.

To determine if in situ annealing could remove residual carbon and oxygen contamination at typical ALD temperatures, annealing was performed at temperatures ranging from  $25 \,^{\circ}$ C to  $450 \,^{\circ}$ C. As shown in Fig. 3(b), the results indicate that the majority of residual oxygen is removed or desorbed at temperatures above 200 °C. The oxygen ratio was reduced to approximately 5% after the 200 °C anneal, which is near the sensitivity limit for the XPS system. However, even after annealing at 450 °C anneal, the carbon remained unchanged. For  $\sim 1200$  eV detected electrons (excitation energy-binding energy), the escape depth is about 10 Å. However, the measurements were taken at a take-off angle of 30° resulting in a XPS probe depth of  $\sim$ 5 Å. Therefore, the C/Ga = 0.2 ratio indicates approximately 0.5 ML carbon contamination. While the majority of residual oxide is removed below the 300 °C ALD temperature, the remaining carbon could impact the ALD nucleation process because TMA will not nucleate on the portions of the surface which are covered by carbon. This is consistent with in situ atomic hydrogen being required to improve the nucleation density.



FIG. 4. In situ XPS study of a sulfur 2s GaN(0001) and GaAs(001) treated with  $(NH_4)_2S$ . Both measurements were taken immediately after loading into the vacuum chamber at room temperature. The GaAs sample which has an S peak while the GaN which does not have an S peak received the  $(NH_4)_2S$  treatment. The bonding between the sulfur and GaN is sufficiently weak to allow for immediate desorption in vacuum.

The reduced coverages of oxygen and carbon in unannealed samples treated with 5%(NH<sub>4</sub>)<sub>2</sub>S compared to samples which only received the HCl and NH4OH clean suggest that the  $(NH_4)_2S$  solution protects the surface from reoxidation.  $(NH_4)_2S$  is known to form a stable sulfur layer on GaAs.<sup>32,36-38</sup> XPS measurements were performed on GaN(0001) samples that received the (NH4)2S wet clean process to determine whether sulfur was present on the surface. Initial measurements for GaN(0001) samples did not indicate the presence of sulfur on the surface as there was no detectable signal for the sulfur peaks or chemical shifts in the rest of the spectra. The use of  $(NH_4)_2S$  is well documented on GaAs,<sup>32, 36–38</sup> so to more diffinitively show that the wet clean process was temporarily preventing surface reoxidation XPS measurements were performed on GaAs(001) samples which received the identical  $(NH_4)_2S$  wet clean. Both samples were measured at room temperature immediately after loading into the chamber, and the results for the GaAs and GaN samples are shown in Fig. 4. These XPS results show a clear sulfur peak for the GaAs sample which had received the  $(NH_4)_2S$ treatment while that same peak is missing for GaN. This discrepency is likely due to weaker bonding between GaN and sufur. In the case of GaN, the bonding between the sulfur and GaN is sufficiently weak to allow for immeadiate desorption in vacuum consistent with the sulfur layer only being stable in the presence of a moist atmosphere. It is assumed that sulfur was bonded to the surface in ambient, because the  $(NH_4)_2S$ treatment resulted in a 2-fold reduction of oxygen prior to in-vacuum annealing as shown in Fig. 3(a).

To experimentally verify the DFT-MD results and examine the effects of the wet and dry cleaning processes on the bonding at the oxide-semiconductor interface, Angle Resolved XPS (ARXPS) was performed on Ga-terminated GaN(0001) samples that underwent 8 cycles of  $Al_2O_3$  ALD. Spectra were taken at a range of exit angles to examine the chemical shifts as the structure transitions from bulk GaN to the  $Al_2O_3/GaN$  interface. The spectra for the Ga 3d peak of the control sample (treatment A) and one which received both



FIG. 5. *Ex situ* angle resolved XPS of a-Al<sub>2</sub>O<sub>3</sub>/GaN(0001) stack. (a) Ga 3d XPS spectra at varying collection angles with respect to the surface normal of the control sample treated with TMA only (treatment A). The curves corresponding to near normal emission ( $26^\circ$ ) and near grazing emission ( $64^\circ$  and combined 71° with 79° spectra) are extracted from (b) experimental angle-resolved spectra by background subtraction and scaling with the factors shown in brackets. (c) and (d) Similar spectra for the sample treated with the (NH<sub>4</sub>)<sub>2</sub>S wet clean as well as cyclic TMA and hydrogen (treatment D). There is no change in the peak energy position versus angle consistent with the absence of a detectable amount of interfacial gallium oxide. The scaling factors for the grazing emission spectra are higher for the spectra ((c) and (d)), that is, the result of a thicker a-Al<sub>2</sub>O<sub>3</sub> after treatment D.

the  $(NH_4)_2S$  ex situ and the in situ cyclic TMA and hydrogen clean (treatment D) are shown in Fig. 5. Note the Ga 3d signal was employed because it has relatively high kinetic energy, which is needed to provide the signal-to-noise ratio required in angle-resolved measurements. However, use of the Ga 3d signal retains the high surface sensitivity, which is clear from strong attenuation of high-angle signal by the oxide layer. In the spectra, the intensity of the Ga 3d peak increases as the collection angle becomes more bulk sensitive, but there is no discernible chemical shift. This indicates that the bulk and surface gallium atoms have identical charge states. This is consistent with the DFT-MD model for the a-Al<sub>2</sub>O<sub>3</sub>/GaN(0001) interface, since the Bader charge calculations show the interfacial, fully bonded gallium atoms are in a nearly bulk-like state. The calculated difference of -0.01|e| in charge between bulk and interfacial atoms is essentially negligible and would not produce a chemical shift detectable by XPS.

Reports in the literature suggest that the difference in charge from bulk GaN to  $Ga_2O_3$  would produce a shift large enough to be detected in the XPS scans. Wolter *et al.* determined that Ga 3d states in  $Ga_2O_3$  have a chemical shift of +1.2 eV on GaN.<sup>39</sup> Surdu-Bob *et al.*<sup>40</sup> determined the Ga 3d chemical shift of gallium suboxide  $Ga_2O$  relative to  $Ga_2O_3$  of

-0.6 eV. Therefore, it is estimated that Ga<sub>2</sub>O has a chemical shift of +0.6 eV relative to bulk GaN.<sup>40</sup> The results of Wolter *et al.*<sup>39</sup> and Surdu-Bob *et al.*<sup>40</sup> show that XPS should readily detect any interfacial oxide or suboxide formation. Thus, the absence of any chemical shift in the spectra for the Ga 3d peak indicates that there is no significant formation of Ga<sub>2</sub>O<sub>3</sub> or Ga<sub>2</sub>O, and that the combined *ex situ* and *in situ* cleaning process have restored the interfacial atoms to a bulk-like configuration. Furthermore, this result is consistent with the DFT-MD model presented in this work.

In a separate study,<sup>41</sup> ALD pretreatments A-D described previously were applied prior to deposition of 80 cycles of  $Al_2O_3$  gate oxide. C-V measurements were employed to determine the effect of the pretreatments of electronic defect states. Interfacial trap densities were calculated using the Terman method and the border trap densities in the oxide were quantified using the method detailed by Taur *et al.*<sup>42</sup> A summary of these results is listed in Table II. Although it is known to lead to potential difficulties in quantitative analysis,<sup>43</sup> the Terman method is currently the most accepted way to characterize the interface states in the nitrides. The Terman method is a useful framework for comparison of different interface state densities based on C-V curve measurements, although the detailed numerical values may be subject to uncertainty.

| TABLE II. | Summary of | of trap | densities |
|-----------|------------|---------|-----------|
|-----------|------------|---------|-----------|

| Pretreatment                   | 8-cycle Al <sub>2</sub> O <sub>3</sub> thickness (nm) <sup>a</sup> | $\mathrm{D}_{\mathrm{it}}(\mathrm{eV}^{-1}\mathrm{cm}^{-2})^{\mathrm{b}}$ | Border traps (eV <sup>-1</sup> cm <sup>-3</sup> ) <sup>b</sup> |
|--------------------------------|--|---|--|
| A (TMA only)                   | 0.62   | $2.8 	imes 10^{12} \pm 1.3\%^{c}$   | $2.0 \times 10^{20} \pm 5.1\%^{c}$                             |
| B (sulfide + TMA)              | 0.56   | $2.0 \times 10^{12} \pm 4.1\%$  | $1.0 	imes 10^{20} \pm 2.8\%$                                  |
| C (hydrogen and TMA)           | 0.87   | $1.1 \times 10^{12} \pm 4.1\%$  | $3.9 	imes 10^{19} \pm 4.5\%$                                  |
| D (sulfide + hydrogen and TMA) | 0.90   | $0.9 \times 10^{12} \pm 4.1\%$  | $2.5 	imes 10^{19} \pm 1.3\%$                                  |

<sup>a</sup>Thicknesses were derived from ARXPS depth profiling.

<sup>b</sup>Trap densities (D<sub>it</sub>) were calculated using the Terman method, at an energy corresponding to 0.5 eV below the conduction band edge. Border traps were evaluated in the accumulation region of the C-V curves Ref. 42.

<sup>c</sup>Error reported is the relative standard error of the mean.

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While the defect levels for all samples are relatively large, the overall trends allow for comparison of each pretreatment. Each pretreatment and ALD was repeated multiple times using the same wafer, precursors, and gasses, allowing for the most direct and reproducible comparison of each pretreatment. The calculations showed that samples that had pretreatments C and D, which included atomic hydrogen in the in situ clean, had the lowest densities of both interfacial traps and border traps. The addition of the sulfur treatment resulted in further, more modest reductions in trap density. One-way Anova model p-value calculations for a sample of devices produced using each pretreatment confirms that the reductions in both D<sub>it</sub> and border trap densities between samples with treatments C and D are significant. Overall, these results indicate that the pre-ALD cleaning process improves the quality of the deposited oxide. More specifically, the reduction in trap density is consistent with an increase in nucleation density, which would result in passivation of the aberrant interfacial bonds that produce trap states. Film thickness values for samples which had only 8 cycles of ALD were derived from the ARXPS depth profiling and are shown in Table II. An increase in nucleation density causes an increase in growth per cycle during the initial stages of growth. The thickness data shows that samples which had the hydrogen plasma cleaning were approximately 40%-60% thicker than samples which did not have that treatment. This is in agreement with the hypothesis that the hydrogen plasma clean reduces trap densities by improving oxide nucleation. However, note that the ARXPS indicated that all samples had low levels of carbon contamination in the films.

The improvement in nucleation density as a result of the surface treatment stems from the removal of the undesirable native oxide and surface contamination which can prevent TMA from chemisorbing. The proposed mechanism begins with the HCl and NH<sub>4</sub>OH solutions dissolving the native oxide. Subsequently dipping in the (NH<sub>4</sub>)<sub>2</sub>S solution terminates the surface with a layer of weakly bound sulfur, which temporarily prevents surface reoxidation. The TMA component of the in situ clean removes any residual oxide or oxygen contamination by essentially acting as a getter. Finally, the role of the critical hydrogen plasma is two-pronged. Atomic hydrogen can reduce carbon species on the surface into volatile compounds which can be pumped out of the system. Additionally, the hydrogen provides a reducing atmosphere that allows the TMA to effectively clean the surface without becoming prematurely oxidized and can prevent background water (or other oxidants or carbon containing species) from interacting with the surface.

#### **IV. CONCLUSION**

Theoretical DFT modeling predicts that gate oxide stacks consisting of  $a-Al_2O_3/O-Ga-O/GaN(0001)$  will produce a nearly ideal interface because the crystalline O-Ga-O layer eliminates all dangling bonds on GaN(0001) and dangling bond defects at the  $Al_2O_3/O$ -Ga-O interface have states outside the band gap of GaN(0001). DFT models of a simpler structure,  $a-Al_2O_3/GaN(0001)$ , in which the amorphous oxide bonds directly to GaN(0001) have an interface with a slightly greater propensity to form defects than a-Al<sub>2</sub>O<sub>3</sub>/O-Ga-O/GaN(0001). However, a-Al<sub>2</sub>O<sub>3</sub> does passivate the GaN(0001) interface if the oxide nucleates in each unit cell and Ga-Al bonds and GaN dangling bonds are eliminated. The a-Al<sub>2</sub>O<sub>3</sub> layer is able to passivate GaN(0001) because the oxide removes the dangling bond states from the surface gallium atoms and restores their bulk-like charge. In contrast to the O-Ga-O/GaN(0001) interface, the dangling and metallic bonds in the direct bonding configuration create midgap states because of the relative weakness of bonds in GaN compared to O-Ga-O. The DFT calculations show that trap states and therefore D<sub>it</sub> can be reduced by providing more "bulk-like" bonding at the interface and removing all dangling bonds and metal-metal bonds. The surface cleans affect this bonding by removing contamination and increasing the density of TMA nucleation sites (increasing the Al2O3 nucleation). To nucleate the bonding in each unit cell, the interface must be free of contamination prior to Al<sub>2</sub>O<sub>3</sub> ALD deposition. XPS results showed that the use of a  $5\%(NH_4)_2S$  after wet etch removal of the native oxide successfully reduced carbon and oxygen contamination as well as prevented reoxidation of the surface prior to loading into the ALD chamber. In contrast to S/InGaAs(001), the sulfur on GaN(0001) desorbs even at 25 °C. XPS experiments show bulk-like bonding at the a-Al<sub>2</sub>O<sub>3</sub>/GaN(0001) interface consistent with DFT models of the Al<sub>2</sub>O<sub>3</sub>/GaN(0001) interface.

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- <sup>1</sup>K. Matocha, T. P. Chow, and R. J. Gutmann, IEEE Trans. Electron Devices **52**(1), 6–10 (2005).
- <sup>2</sup>M. Lachab, M. Sultana, H. Fatima, V. Adivarahan, Q. Fareed, and M. Khan, Semicond. Sci. Technol. **27**(12), 125001 (2012).
- <sup>3</sup>R. Vetury, N. Q. Zhang, S. Keller, and U. K. Mishra, IEEE Trans. Electron Devices **48**(3), 560–566 (2001).
- <sup>4</sup>D. Segev and C. Van de Walle, EPL (Europhys. Lett.) **76**(2), 305 (2006).
- <sup>5</sup>M. Fagerlind, F. Allerstam, E. O. Sveinbjornsson, N. Rorsman, A. Kakanakova-Georgieva, A. Lundskog, U. Forsberg, and E. Janzen, J. Appl. Phys. **108**(1), 014508 (2010).
- <sup>6</sup>N. Ramanan, B. Lee, C. Kirkpatrick, R. Suri, and V. Misra, Semicond. Sci. Technol. 28(7), 074004 (2013).
- <sup>7</sup>Y. C. Chang, W. H. Chang, H. C. Chiu, L. T. Tung, C. H. Lee, K. H. Shiu, M. Hong, J. Kwo, J. M. Hong, and C. C. Tsai, Appl. Phys. Lett. **93**(5), 053504 (2008).
- <sup>8</sup>D. A. Deen, D. F. Storm, R. Bass, D. J. Meyer, D. S. Katzer, S. C. Binari,
- J. W. Lacis, and T. Gougousi, Appl. Phys. Lett. 98, 023506 (2011).
  P. D. Ye, B. Yang, K. K. Ng, J. Bude, G. D. Wilk, S. Halder, and J. C. M.
- Hvang, Appl. Phys. Lett. **86**(6), 063501 (2005).
- <sup>10</sup>S. Gu, H. Katayose, K. Nomoto, T. Nakamura, A. Ohoka, K. Lee, W. Lu, and P. M. Asbeck, Phys. Status Solidi C **10**(5), 820–823 (2013).
- <sup>11</sup>T. Hashizume, S. Ootomo, and H. Hasegawa, Appl. Phys. Lett. 83(14), 2952–2954 (2003).
- <sup>12</sup>T. Hashizume, S. Ootomo, T. Inagaki, and H. Hasegawa, J. Vac. Sci. Tech. B 21(4), 1828 (2003).
- <sup>13</sup>M. Esposto, S. Krishnamoorthy, D. N. Nath, S. Bajaj, T.-H. Hung, and S. Rajan, Appl. Phys. Lett. **99**(13), 133503 (2011).
- <sup>14</sup>A. N. Hattori, K. Endo, K. Hattori, and H. Daimon, Appl. Surf. Sci. 256(14), 4745–4756 (2010).

- <sup>15</sup>A. N. Hattori, F. Kawamura, M. Yoshimura, Y. Kitaoka, Y. Mori, K. Hattori, H. Daimon, and K. Endo, Surf. Sci. 604(15), 1247–1253 (2010).
- <sup>16</sup>B. Brennan, X. Qin, H. Dong, J. Kim, and R. M. Wallace, Appl. Phys. Lett. 101(21), 211604 (2012).
- <sup>17</sup>A. D. Carter, W. J. Mitchell, B. J. Thibeault, J. J. Law, and M. J. Rodwell, Appl. Phys. Express 4(9), 091102 (2011).
- <sup>18</sup>E. R. Cleveland, L. B. Ruppalt, B. R. Bennett, and S. Prokes, Appl. Surf. Sci. 277, 167–175 (2013).
- <sup>19</sup>L. B. Ruppalt, E. R. Cleveland, J. G. Champlain, S. M. Prokes, J. Brad Boos, D. Park, and B. R. Bennett, Appl. Phys. Lett. **101**(23), 231601– 231605 (2012).
- <sup>20</sup>C. L. Hinkle, A. M. Sonnet, E. M. Vogel, S. McDonnell, G. J. Hughes, M. Milojevic, B. Lee, F. S. Aguirre-Tostado, K. J. Choi, H. C. Kim, J. Kim, and R. M. Wallace, Appl. Phys. Lett. **92**(7), 071901 (2008).
- <sup>21</sup>G. Kresse and J. Furthmüller, Computat. Mater. Sci. 6(1), 15–50 (1996).
- <sup>22</sup>G. Kresse and J. Furthmüller, Phys. Rev. B **54**(16), 11169 (1996).
- <sup>23</sup>G. Kresse and D. Joubert, Phys. Rev. B **59**(3), 1758 (1999).
- <sup>24</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**(18), 3865 (1996).
- <sup>25</sup>P. E. Blöchl, Phys. Rev. B **50**(24), 17953 (1994).
- <sup>26</sup>E. A. Chagarov and A. C. Kummel, J. Chem. Phys. **135**(24), 244705– 244717 (2011).
- <sup>27</sup>J. Heyd and G. E. Scuseria, J. Chem. Phys. **121**(3), 1187–1192 (2004).
- <sup>28</sup>J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**(18), 8207– 8215 (2003).
- <sup>29</sup>J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**(21), 219906 (2006).
- <sup>30</sup>M. Yokoyama, N. Taoka, R. Suzuki, O. Ichikawa, H. Yamada, N. Fukuhara, M. Hata, M. Sugiyama, Y. Nakano, M. Takenaka, and S. Takagi, in

- <sup>31</sup>N. Goel, P. Majhi, C. O. Chui, W. Tsai, D. Choi, and J. S. Harris, Appl. Phys. Lett. **89**(16), 163517 (2006).
- <sup>32</sup>P. T. Chen, Y. Sun, E. Kim, P. C. McIntyre, W. Tsai, M. Garner, P. Pianetta, Y. Nishi, and C. O. Chui, J. Appl. Phys. **103**(3), 034106 (2008).
- <sup>33</sup>J. Son, V. Chobpattana, B. M. McSkimming, and S. Stemmer, Appl. Phys. Lett. **101**(10), 102905 (2012).
- <sup>34</sup>V. Chobpattana, J. Son, J. J. Law, R. Engel-Herbert, C.-Y. Huang, and S. Stemmer, Appl. Phys. Lett. **102**(2), 022907 (2013).
- <sup>35</sup>Y. Dong, R. M. Feenstra, and J. E. Northrup, J. Vac. Sci. Technol. B 24, 2080 (2006).
- <sup>36</sup>M. Milojevic, C. L. Hinkle, F. S. Aguirre-Tostado, H. C. Kim, E. M. Vogel, J. Kim, and R. M. Wallace, Appl. Phys. Lett. **93**(25), 252905 (2008).
- <sup>37</sup>F. S. Aguirre-Tostado, M. Milojevic, K. J. Choi, H. C. Kim, C. L. Hinkle, E. M. Vogel, J. Kim, T. Yang, Y. Xuan, P. D. Ye, and R. M. Wallace, Appl. Phys. Lett. **93**(6), 061907 (2008).
- <sup>38</sup>H. Sik, Y. Feurprier, C. Cardinaud, G. Turban, and A. Scavennec, J. Electrochem. Soc. **144**(6), 2106–2115 (1997).
- <sup>39</sup>S. Wolter, B. Luther, D. Waltemyer, C. Onneby, S. Mohney, and R. Molnar, Appl. Phys. Lett. **70**(16), 2156–2158 (1997).
- <sup>40</sup>C. Surdu-Bob, S. Saied, and J. Sullivan, Appl. Surf. Sci. **183**(1), 126–136 (2001).
- <sup>41</sup>S. Gu, A. J. Kerr, E. Chagarov, A. C. Kummel, and P. M. Asbeck, paper presented at the 60th AVS Annual Meeting, Long Beach, CA, 2013.
- <sup>42</sup>Y. Yuan, L. Wang, B. Yu, B. Shin, J. Ahn, P. C. McIntyre, P. M. Asbeck, M. J. Rodwell, and Y. Taur, IEDL **32**(4), 485 (2011).
- <sup>43</sup>See supplementary material at http://dx.doi.org/10.1063/1.4894541 for DFT-MD results describing Al<sub>2</sub>O<sub>3</sub> passivation of the N-polar GaN(0001).