

Annual Report for AOARD Grant FA2386-11-1-4077
"Device Performance and Reliability Improvements of AlGaN/GaN/Si MOSFET
Using Defect-Free Gate Recess and Laser Annealing"

July 18, 2012

Name of Principal Investigators: Robert M. Wallace

- e-mail address : rmwallace@utdallas.edu
- Institution : University of Texas at Dallas
- Mailing Address : 800 W. Campbell Road, RL10
- Phone : 972-883-6638
- Fax : 972-883-5725

Period of Performance: 07/26/2011 – 07/26/2012

Abstract: In-situ studies were conducted of atomic layer deposition (ALD) of Al_2O_3 on GaN and $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$ (AlGaN) substrates. For GaN substrates, it was found that O_3 exposure at 400°C results in adequate functionalization of the GaN surface to enable subsequent ALD growth of Al_2O_3 in a much shorter incubation period relative to a HF-treated GaN surface, and the O_3 exposure also results in detectable N-O bonding. In contrast to III-arsenide-based substrates, no detectable Ga-oxide reduction "clean-up" effect is observed for the GaN surface. For AlGaN, it is found that Al_2O_3 , Ga_2O_3 and N-O states were detected on native oxide and HF-treated surfaces. During the course of the ALD process, the N-O bonds are seen to decrease to a level near XPS detection limits, as well as a small decrease in the Ga_2O_3 concentration, consistent with a "clean-up" effect. The Al_2O_3 growth rate initially is seen to be very low relative to other III-V substrates, and is again an indication of low reactivity between the TMA molecule and the AlGaN surface. However, this rate on AlGaN is higher than that observed for a GaN substrate, indicating that the presence of the Al on the AlGaN surface alters the reaction efficiency during ALD, rendering Al-O bonding more favorable and thus subsequent Al_2O_3 growth.

Introduction: Due to the large bandgap and relatively high mobility of III-V nitride-based materials, there is significant interest in the fabrication of nitride-based high electron mobility transistors (HEMTs) and other high power, high frequency and high temperature devices.^{1,2} However, these are known to experience significant surface related effects, such as large leakage currents³ and frequency dependent current collapse.⁴ One of the proposed methods to improve these devices is through the fabrication of metal-oxide-semiconductor HEMTs or hetero-field-effect-transistors (MOS-HEMTs or MOS-HFETs) by incorporating a high-dielectric constant (high-k) oxide layer between the semiconductor and the gate metal.^{5,6} This would have the effect of significantly reducing leakage current, potentially improving mobility by preventing degradation of the semiconductor surface, and through passivation of the surface preventing current collapse by suppression of electron trapping at surface states, thereby providing increased reliability of MOS-HEMT based devices.^{7,8} In terms of high-k deposition on these surfaces, atomic layer deposition (ALD) provides the most likely candidate for advanced device fabrication, due to the potential for high sample through put, controlled growth rates and high aspect ratio conformal growth.

A number of studies have looked at the effect of different wet chemical treatments at removing native oxides and surface contamination from III-V nitride surfaces.^{9, 10} Hydrofluoric acid (HF) etching of GaN surfaces has previously been shown to produce one of the lowest oxide concentrations when compared to various other wet chemical treatments,¹¹ with only HCl seen to produce a marginally more oxide free surface.¹² Previous studies

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 20 JUL 2012		2. REPORT TYPE Annual		3. DATES COVERED 19-07-2011 to 18-07-2012	
4. TITLE AND SUBTITLE Device Performance and Reliability Improvements of AlGa_N/Ga_N/Si MOSFET Using Defect-Free Gate Recess and Laser Annealing			5a. CONTRACT NUMBER FA23861114077		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Robert Wallace			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Texas at Dallas, 800 W Campbell Rd, RL 10, Richardson, TX, 75080			8. PERFORMING ORGANIZATION REPORT NUMBER N/A		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD, UNIT 45002, APO, AP, 96338-5002			10. SPONSOR/MONITOR'S ACRONYM(S) AOARD		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) AOARD-114077		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This is the first annual report on in-situ studies conducted of atomic layer deposition (ALD) of Al₂O₃ on GaN and Al_{0.25}Ga_{0.75}N (AlGa_N) substrates. For GaN substrates, it was found that O₃ exposure at 400°C results in adequate functionalization of the GaN surface to enable subsequent ALD growth of Al₂O₃ in a much shorter incubation period relative to a HF-treated GaN surface, and the O₃ exposure also results in detectable N-O bonding. In contrast to III-arsenide-based substrates, no detectable Ga-oxide reduction ?clean-up? effect was observed for the GaN surface.					
15. SUBJECT TERMS nano technology, Power-efficient System-on-Chip, AlGa_N/Ga_N/Si					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

looking at $\text{SiN}_x/\text{Al}_2\text{O}_3/\text{AlGaIn}/\text{GaIn}$ heterostructures showed low D_{it} levels at the oxide/semiconductor interface,¹³ and using a high-k $\text{LaAlO}_3/\text{SiO}_2$ bi-layers also on $\text{AlGaIn}/\text{GaIn}$ structures, high drive currents, low threshold voltages, and high mobility was achieved with a capacitance extracted thickness for the high-k of 3 nm.¹⁴ However, very little is reported about the interfacial chemistry that takes place between deposited high-k materials and III-V nitride surfaces.¹⁵ For this reason, this research examines the effect of depositing Al_2O_3 by ALD on GaN and $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$ surface, with X-ray photoelectron spectroscopy (XPS) carried out after successive “half cycles” of the ALD process,¹⁶ to monitor the chemical changes at the semiconductor/high-k interface. Ultimately, our goal to establish correlations between the interfacial chemistry seen and the electrical performance of nitride-based MOS devices with our AOARD program partners at National Chiao Tung University (Prof. A. Chin).

Experiment: For the GaN studies, metalorganic chemical vapor deposition (MOCVD) grown n-GaN on sapphire was used as the substrate. The surfaces were pre-cleaned using a solvent degreasing step (acetone/iso-propanol/ H_2O for 2 min each), wet chemical cleaning (2% HF for 2 min followed by 2 min H_2O rinse) and blown dry with N_2 .¹⁷ Immediately after surface preparation, the samples were loaded in an ultra high vacuum (UHV) custom tool with an integrated monochromatic Al $K\alpha$ XPS ($h\nu = 1486.7$ eV) and a Picosun SUNALE[®] ALD reactor as described in detail elsewhere.¹⁸ Briefly, the UHV system consists of a number of vacuum chambers, each providing capabilities for various UHV deposition or characterization techniques, coupled together through a UHV “backbone transfer tunnel” maintained at a pressure of $<1 \times 10^{-10}$ mbar, to allow for analysis after deposition without exposure to atmospheric conditions, which can introduce deleterious contamination and interfacial oxidation. The ALD reactor is integrated to the UHV backbone through an intermediate “buffer chamber” to span the pressures between the reactor and the transfer tunnel. TMA from SAFC Hi-tech[®] was used as the metal precursor. De-ionized water (resistivity of ~ 18 M Ω) vapor was used as the oxidant. O_3 with a concentration of 380 g/m³ was used for GaN substrate oxidation at 400°C, for 30 minutes inside the ALD reactor. The temperature of the ALD reactor was maintained at 300 °C during ALD. The base pressure of the ALD reactor was ~ 12 mbar and ultrahigh purity nitrogen (N_2 , 99.999%) was used as the purge gas during depositions. The TMA- and H_2O -injection pulse times were both 1s, respectively. In-situ XPS was obtained after each TMA or H_2O half-cycle reaction on the HF-treated and O_3 -oxidized GaN. The XPS data was charge referenced to the N 1s (397.9 eV) core level from the GaN substrate.¹⁹

For the AlGaIn studies, undoped $\text{Al}_{0.25}\text{Ga}_{0.75}\text{N}$ (30 nm) samples, grown on a 1.2 μm GaN layer on a Si(111) substrate from DOWA Electronics Materials, were first solvent cleaned in acetone, methanol and isopropanol for one minute each. One sample was then etched in a 2% HF solution for 2 minutes, followed by a 2 minute rinse in flowing deionized water and dried with nitrogen. The sample was then immediately mounted to a sample plate along with an un-etched sample and introduced to the same UHV. In this study, ALD of Al_2O_3 was also carried out on the AlGaIn surfaces at a substrate temperature of 300 °C. Trimethyl-aluminum (TMA) and H_2O were used as the precursors for ALD, with a precursor pulse and purge time of 0.1 and 4 s respectively.

Results and Discussion:

GaN studies

Figure 1 shows the cross-sectional transmission electron micrograph of the post-ALD samples for (a) HF-treated and (b) O_3 -treated GaN substrate. An approximately 1.5–2 nm thick lighter contrast layer is evident for the O_3 -oxidized GaN substrate indicative of GaO(N) growth at the GaN surface, while no detectable growth is observed for the HF-treated

surface. Figure 1(c) shows the normalized Ga $2p_{3/2}$ XPS for HF treated and O₃-oxidized GaN substrates. The area under the Ga $2p_{3/2}$ peak for HF-treated GaN is shaded for comparison with the O₃-oxidized GaN. An increase in the FWHM (full width at half maximum) by ~0.4 eV relative to the HF etched sample is seen after O₃-oxidation. This increase in peak width is clearly indicative of an increase in GaO(N) bonding at a higher binding energy (~0.4 eV) in addition and relative to the GaN substrate bonding (~1118.3 eV) upon O₃-oxidation.²⁰ Although the low oxidation temperature of 400 °C should not substantially oxidize GaN, the presence of O₃ as the oxidant is expected to cause aggressive oxidation of GaN. Such aggressive oxidation by O₃ was previously shown by Brennan *et al.* where O₃ caused formation of thicker Ga-oxides on InGaAs even after the 1st O₃ half-cycle during ALD Al₂O₃ growth.²¹ Figure 1(inset) shows the O 1s raw data for the corresponding samples. For HF-treated GaN, two distinct bonds are seen: O–H (~533.35 eV) and possibly Ga–O–N (~531.85 eV), whereas a near symmetric peak at ~531.5 eV indicating a predominantly single bonding environment is seen for O₃-oxidized GaN.

Figure 2 shows the corresponding Al $2p$ region for the samples. It is evident that the O₃ oxidation treatment dramatically impacts the surface reactivity enabling more rapid nucleation and growth of the Al₂O₃ layer.

These results indicate that O₃-oxidation is an effective method to enable a more rapid incubation and nucleation of Al₂O₃ growth by ALD. Further details of the study are presented in the publication listed below. Future plans include the examination of the O₃ process on higher-k dielectric growth, such as HfO₂, on GaN.

AlGaN studies

Based on the total oxygen concentration on the two samples upon introduction to UHV from the O 1s spectra (not shown), etching of the sample in HF reduced the concentration of oxygen by >40% relative to that seen on the native oxide sample. In order to determine where these changes to the substrate-oxide bonding were taking place, it was necessary to look at Ga, N and Al core level spectra in more detail. The peak fitted Ga $2p_{3/2}$ and N 1s spectra after each individual stage in the deposition process are shown in Figure 3. The Ga $2p$ spectra in Figure 3(a) and (b) for the native oxide and HF etched samples respectively, show evidence of two peaks; one at 1117.5 eV assigned to Ga bonded to AlN, and the other at 1118.2 eV, indicative of a Ga 3+ oxidation state, likely due to Ga₂O₃, consistent with previous reports.^{22,23} There is no evidence of a Ga 1+ state, however detection of this state is complicated due to the Ga-AlN peak having a similar binding energy to that of the Ga₂O

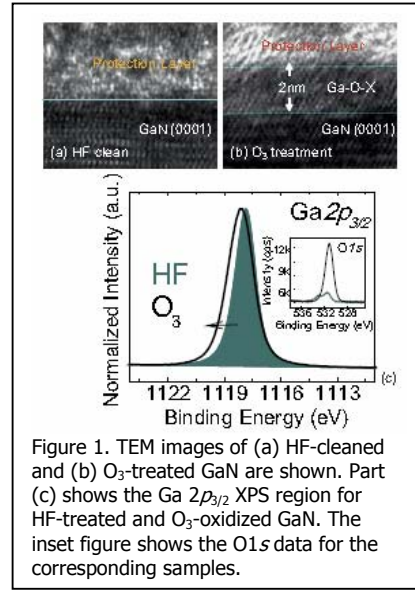


Figure 1. TEM images of (a) HF-cleaned and (b) O₃-treated GaN are shown. Part (c) shows the Ga $2p_{3/2}$ XPS region for HF-treated and O₃-oxidized GaN. The inset figure shows the O 1s data for the corresponding samples.

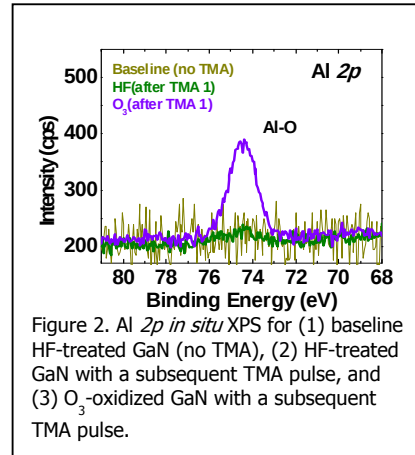


Figure 2. Al $2p$ *in situ* XPS for (1) baseline HF-treated GaN (no TMA), (2) HF-treated GaN with a subsequent TMA pulse, and (3) O₃-oxidized GaN with a subsequent TMA pulse.

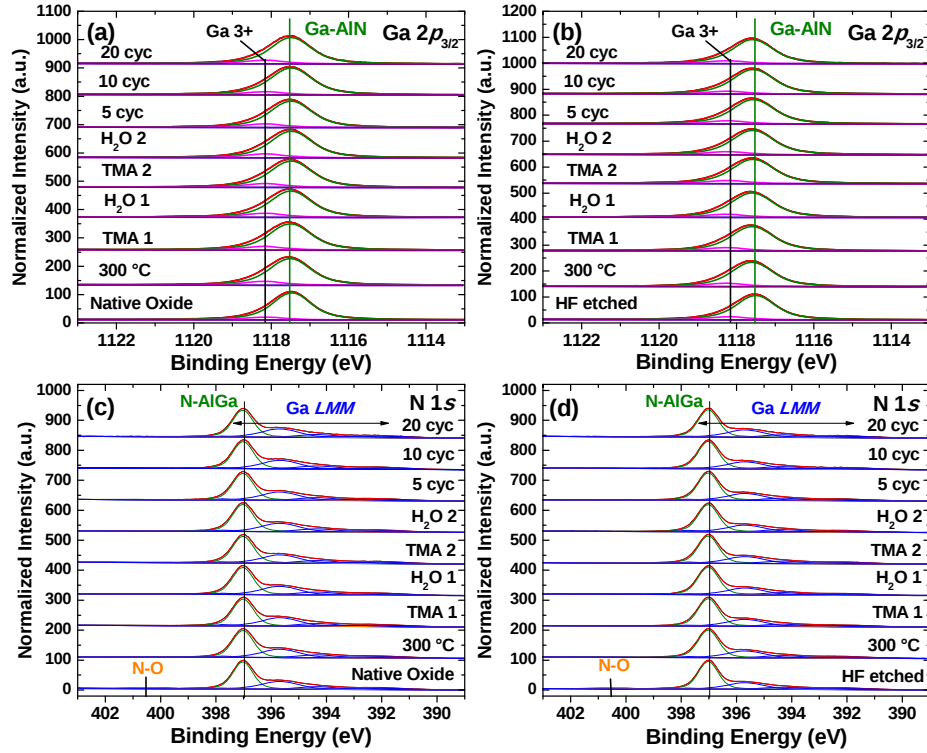


Figure 3. XPS spectra of the Ga $2p_{3/2}$ (a, b) and N $1s$ (c, d) core levels from the native oxide (a, c) and HF etched (b, d) surfaces, from the initial surfaces, after annealing at 300 °C and each individual ALD half cycle deposition.

peak (1117.55 eV), as seen on GaAs and InGaAs samples.²⁴ Upon heating of the samples to 300 °C in the ALD reactor there is a slight broadening of the Ga-AlN peak, such that the FWHM increases from 1.03 eV to 1.11 eV, which persists during subsequent ALD cycles. This could be evidence for formation of a low concentration of lower binding energy oxidation states or general disorder at the AlGaN surface.

The corresponding N $1s$ spectra in Figure 3(c) and (d) show the N-AlGa peak at 397.0 eV,²⁵ a N-O peak at ~400.5 eV,²⁶ as well as the Ga $L_{25}M_{45}M_{45}$ Auger feature (~392-398 eV). The Auger feature is fitted in such a way that the line-shape remains constant throughout and is consistent with line-shapes from previously reported spectra.²⁷ It should be pointed out that the commonly reported GaN-O bond at ~398 eV is likely to be a component of the Ga LMM Auger line, with an increase in this region usually appearing upon gallium oxidation.

In order to show the changes in these spectra more clearly, the Ga $2p$ and N $1s$ core level spectra from the initial surfaces, after 300 °C anneal and after the first TMA pulse, are shown in Figure 4. Upon the first pulse of TMA, it is difficult to detect any obvious change in the Ga $2p$ spectra, however from the ratio of the Ga 3+ peak area to that of the bulk peak, plotted in figure 4(e), we find that there is a slight decrease in the concentration of Ga-O present on the surface as a result of interaction with TMA molecule. This is consistent with the “clean up” effect seen on other III-V semiconductors,²⁸ however the extent of this interaction is much less on these surfaces, suggesting that there is a stronger bond between the Ga 3+ state and AlGaN surface than with other materials. This inherent stability is also

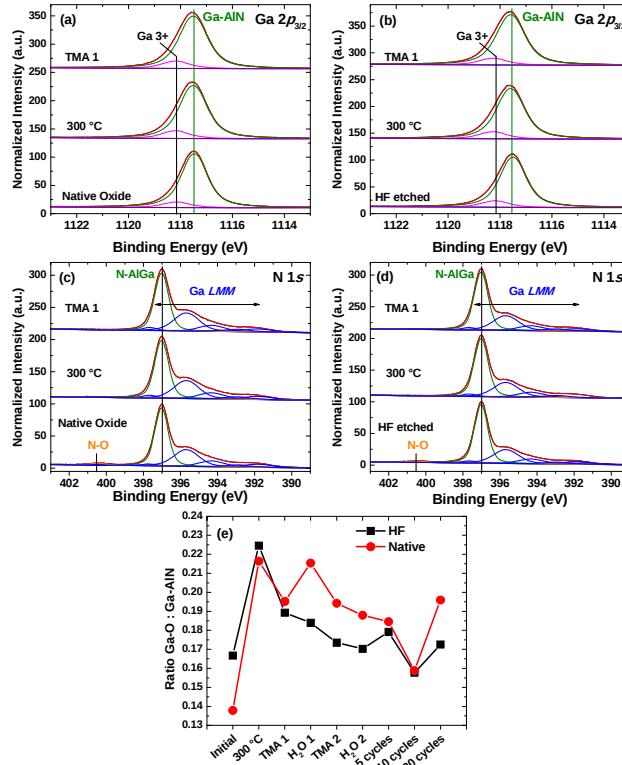


Figure 4. XPS spectra of the Ga 2p_{3/2} (a, b) and N 1s (c, d) core levels from the native oxide (a, c) and HF etched (b, d) surfaces, from the initial surfaces, after annealing at 300 °C and after one pulse of TMA. (e) the ratio of gallium oxide to the bulk Ga-AlN peak from the Ga 2p spectra, indicating the changes in the gallium oxide present on the surface over the course of the deposition.

reflected in the oxide ratios when comparing the native oxide and HF etched surfaces, with the oxide ratio initially seen to be greater on the HF etched surface. This inherent stability is also reflected in GaN studies described above. However, in contrast to the studies on GaN, an incremental decrease in the Ga-O:Ga-AlN ratio is detected with successive cycles of TMA, which is indicative of the “clean up” effect taking place. However, after 20 full cycles, the ratio is seen to increase again, with the highest level seen on the native oxide sample. From the N 1s spectra in figure 4(c) and (d), we find that the N-O signal reduces to within detection limits after introduction to the ALD reactor at 300 °C. This is concurrent with an increase in gallium and aluminum oxide peaks, suggesting oxygen is transferring from the N-O bonding environments to form gallium and aluminum oxide. No further changes are detected in the N 1s spectra throughout the remainder of the deposition process.

The Al 2p spectra for the complete deposition process is presented in Figure 5(a) and (b), and for the 300 °C annealed, after first “half cycle” of TMA and after 20 full cycles spectra in (c) and (d). An Al-GaN bulk peak at 73.5 eV is detected, as well as trace amounts of Al₂O₃ at 74.4 eV. This is present on both the native oxide and HF etched surface initially and is observed to increase upon annealing, shown most clearly in the ratio of oxide to the bulk peaks in Figure 5(e). Subsequently we detect an incremental increase in the Al₂O₃ peak after each successive TMA pulse, as indicated by the plot inset in Figure 5(e) showing the change in ratio during the initial stages of growth. However, this growth rate is much lower than typically expected from other III-V compounds. From XPS thickness calculations based on the attenuation of the Ga 2p peak upon Al₂O₃ deposition, we detect < 0.1 nm of Al₂O₃

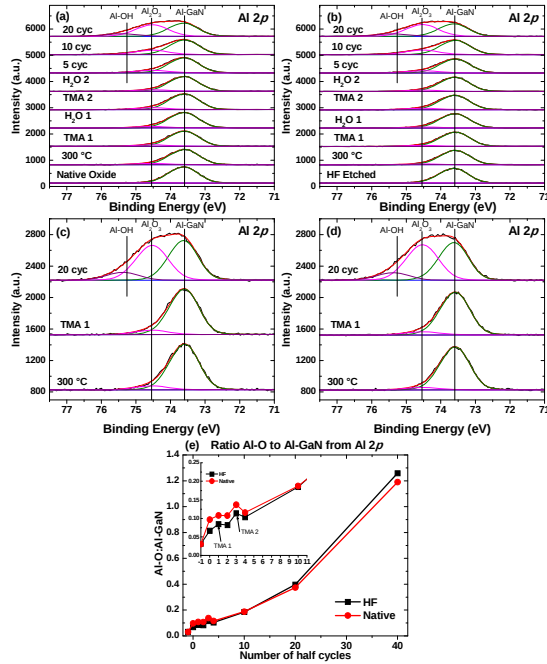


Figure 5. Al 2*p* core level spectra from the native oxide (a, c) and HF etched (b, d) samples at various stages in the Al₂O₃ deposition process. (e) The ratio of Al-O to Al-GaN from the same spectra indicating the change in Al₂O₃ growth rate with increasing number of ALD cycles. Inset shows the change in ratio during the initial ALD cycles.

growth on both surfaces after 5 full cycles. With a further 5 full cycles, a similar growth rate is seen with ~ 0.2 nm of Al₂O₃ detected. However, after the next 10 cycles (20 total) the growth rate is observed to increase significantly, such that the final calculated thickness is 0.9 nm on the native oxide sample and 1.0 nm on the HF etched sample. This suggests that true ALD growth does not occur until a complete monolayer of oxide is formed on the surface and a number of ALD cycles are needed to instigate this growth. This variation in Al₂O₃ thickness on the two samples is further confirmed by the Al-O to Al-GaN ratio in Figure 5(e), with a greater final value observed for the HF etched sample, despite an initially higher ratio seen on the native oxide sample. With increasing Al₂O₃ thickness, the emergence of a higher binding energy peak in the Al 2*p* spectra, at ~ 75.3 eV, takes place, which suggests that there is some Al-OH incorporation into the films. A peak at 532.8 eV in the O 1*s* spectra (not shown) on both samples, also suggests the presence of an -OH related state on both samples.

These results suggest that the AlGaN surface is chemically very stable and that a number (>10) of ALD cycles are needed to initially nucleate the surface with Al₂O₃ before ALD growth is seen to take place. There is evidence of the ALD "clean up" effect taking place, with a decrease in the concentration of gallium oxide states seen upon interaction with the TMA molecule; however this is not sufficient to fully remove the native oxides from the Al₂O₃/AlGaN interface. Future plans include the examination of the ALD process on higher-*k* dielectric growth, such as HfO₂, on AlGaN.

Correlation of the interfacial chemistry and electrical performance of devices with such gate stack dielectrics will be sought with our Taiwanese partner in the program.

List of Publications:

Publications:

P. Sivasubramani, T.J. Park, B. E. Coss, A. Lucero, J. Huang, B. Brennan, Y. Cao, D. Jena, H. Xing, R.M. Wallace, and J. Kim,
"In-situ X-ray photoelectron spectroscopy of trimethyl aluminum and water half-cycle treatments on HF-treated and O₃-oxidized GaN substrates,"
Physica Status Solidi Rapid Research Letters, **6**, 22 (2012).

B. Brennan, X. Qin, H. Dong, J. Kim, and R. M. Wallace,
"In situ atomic layer deposition half cycle study of Al₂O₃ growth on AlGaIn,"
In preparation (2012).

Presentations:

"X-ray photoelectron spectroscopy study of Al₂O₃ deposition by ALD on native oxide and HF etched AlGaIn," R.M.Wallace
9th Taiwan/U.S. Air Force Nanoscience Workshop, Kenting, Taiwan
April 17-20, 2012

¹ S. J. Pearton and F. Ren, Adv. Mater **12**, 1571 (2000)

² S. Strite and H. Morkoc, J. Vac. Sci. Technol. B **10**, 1237 (1992).

³ J. W. Chung, J. C. Roberts, E. L. Piner, and T. Palacios IEEE Electron Device Lett. **29**, 1196 (2008).

⁴ B. M. Green, K. K. Chu, E. M. Chumbes, J. A. Smart, J. M. Shealy, and L. F. Eastman, IEEE Electron Device Lett. **21**, 268 (2000).

⁵ A. L. Corrión, K. Shinohara, D. Regan, I. Milosavljevic, P. Hashimoto, P. J. Willadsen, A. Schmitz, S. J. Kim, C. M. Butler, D. Brown, S. D. Burnham, and M. Micovic, IEEE Electron Device Lett. **32**, 1062 (2011).

⁶ T. Huang, X. Zhu, K. M. Wong, and K. M. Lau, IEEE Electron Device Lett. **33**, 212 (2012).

⁷ T. Mizutani, Y. Ohno, M. Akita, S. Kishimoto, and K. Maezawa, IEEE T. Electron. Dev. **50**, 2015 (2003).

⁸ Y. Ohno, T. Nakao, S. Kishimoto, K. Maezawa, and T. Mizutani, Appl. Phys. Lett. **84**, 2184 (2004).

⁹ M. Diale, F.D. Aureta, N.G. van der Berga, R.Q. Odendaala, and W.D. Roos, Appl. Surf. Sci. **246**, 279 (2005).

¹⁰ H. Ishikawa, S. Kobayashi, Y. Koide, S. Yamasaki, S. Nagai, J. Umezaki, M. Koike, M. Murakami, J. Appl. Phys. **81**, 1315 (1997).

¹¹ S. W. King, J. P. Barnak, M. D. Bremser, K. M. Tracy, C. Ronning, R. F. Davis, and R. J. Nemanich, J. Appl. Phys. **84**, 5248 (1998).

¹² R. Sohal, P. Dudekb, and O. Hilt, Appl. Surf. Sci. **256**, 2210 (2010).

¹³ M. Miczek, C. Mizue, T. Hashizume, and B. Adamowicz, J. Appl. Phys. **103**, 104510 (2008).

¹⁴ C. Y. Tsai, T. L. Wu, and A. Chin, IEEE Electron Device Lett. **33**, 35 (2012).

-
- ¹⁵ P. Sivasubramani, T. J. Park, B. E. Coss, A. Lucero, J. Huang, B. Brennan, Y. Cao, D. Jena, H. Xing, R.M. Wallace, and J. Kim, *Phys. Status Solidi RRL* **6**, 22 (2012).
- ¹⁶ 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**, 252905 (2008).
- ¹⁷ Z. H. Liu, G. I. Ng, H. Zhou, S. Arulkumaran, and Y. K. T. Maung, *Appl. Phys. Lett.* **98**, 113506 (2011).
- ¹⁸ R. M. Wallace, *Electrochem. Soc. Trans.* **16**(5), 255 (2008).
- ¹⁹ J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin Elmer Co., 1992).
- ²⁰ S. D. Wolter, B. P. Luther, D. L. Waltemyer, C. Önnby, S. E. Mohny, and R. J. Molnar, *Appl. Phys. Lett.* **70**(16), 2156 (1997).
- ²¹ B. Brennan, M. Milojevic, H. C. Kim, P. K. Hurley, J. Kim, G. Hughes, and R. M. Wallace, *Electrochem. Solid State Lett.* **12**(6), H205 (2009).
- ²² C. L. Hinkle, M. Milojevic, B. Brennan, A. M. Sonnet, F. S. Aguirre-Tostado, G. J. Hughes, E. M. Vogel, and R. M. Wallace, *Appl. Phys. Lett.* **94**, 162101 (2009).
- ²³ 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**, 071901 (2008).
- ²⁴ C. L. Hinkle, E. M. Vogel, P. D. Ye, and R. M. Wallace, *Curr. Opin. Solid State Mater. Sci.* **15**, 188 (2011).
- ²⁵ F. González-Posada, J. A. Bardwell, S. Moisa, S. Haffouz, H. Tang, A. F. Braña, and E. Muñoz, *Appl. Surf. Sci.* **253**, 6185 (2007).
- ²⁶ J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division (1992).
- ²⁷ E. Antonides, E. C. Janse, and G. A. Sawatzky, *Phys. Rev. B*, **15**, 1669 (1977).
- ²⁸ P. D. Ye, G. D. Wilk, B. Yang, J. Kwo, S. N. G. Chu, S. Nakahara, H.-J. L. Gossman, J. P. Mannaerts, M. Hong, K. K. Ng, and J. Bude, *Appl. Phys. Lett.* **83**, 180(2003).