In situ plasma enhanced atomic layer deposition half cycle study of Al$_2$O$_3$ on AlGaN/GaN high electron mobility transistors

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(Received 28 May 2015; accepted 19 August 2015; published online 28 August 2015)

A half cycle study of plasma enhanced atomic layer deposited (PEALD) Al$_2$O$_3$ on AlGaN is investigated using in situ X-ray photoelectron spectroscopy, low energy ion scattering, and ex situ electrical characterizations. A faster nucleation or growth is detected from PEALD relative to purely thermal ALD using an H$_2$O precursor. The remote O$_2$ plasma oxidizes the AlGaN surface slightly at the initial stage, which passivates the surface and reduces the OFF-state leakage. This work demonstrates that PEALD is a useful strategy for Al$_2$O$_3$ growth on AlGaN/GaN devices.

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Metal insulator semiconductor AlGaN/GaN high electron mobility transistors (MISHEMTs) are promising for power device applications due to a lower leakage current than the conventional Schottky AlGaN/GaN HEMTs. Among a large number of insulator materials, an Al$_2$O$_3$ dielectric layer, deposited by atomic layer deposition (ALD), is often employed as the gate insulator because of a large band gap (and the resultant high conduction band offset on AlGaN), high breakdown field, conformal growth, and a relatively high dielectric constant. In the past decade, much work has been done to study the device performance, as well as the interface chemistry for Al$_2$O$_3$/AlGaN/GaN MISHEMTs. Although an ALD Al$_2$O$_3$ insulator layer grown by Tri-Methyl-Aluminum (TMA) and H$_2$O precursors decreases the leakage current significantly, the ALD Al$_2$O$_3$ is not effective in the passivation of the native AlGaN surface or reduction of the interface state density ($D_{it}$), as well as the interface chemistry for Al$_2$O$_3$/AlGaN/GaN. Moreover, due to a high density of positive charges at the AlGaN surface, an undesirable negative threshold voltage shift appears after the ALD Al$_2$O$_3$. Recently, numerous reports support that the oxidation of AlGaN can decrease the positive interface charges as well as the $D_{it}$. Our recent work also demonstrates that a remote O$_2$/N$_2$ plasma exposure at 550 °C is an available passivation method prior to ALD Al$_2$O$_3$. In contrast, O$_2$ plasma pretreatments under different conditions (flow, time, temperature, etc.) may result in surface damage and a threshold voltage instability ($\Delta V > 1 V$). It is well known that plasma enhanced atomic layer deposition (PEALD) can grow an oxide layer using an oxygen plasma to replace the H$_2$O precursor. Recently, work by Meunier et al. shows that PEALD Al$_2$O$_3$ is able to enhance device performance. However, whether this improvement is relative to the surface oxidation or the Al$_2$O$_3$ film is unclear. In this work, a comparison of purely thermal ALD and PEALD is performed to study the impact of the O$_2$ plasma ambient on the AlGaN surface using in situ X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). Ex situ Capacitance-Voltage (C-V) and Current-Voltage (I-V) measurements are exploited to evaluate the associated device performance.

Undoped (0001) Al$_{0.25}$Ga$_{0.75}$N samples (30 nm), grown on a 1.2 μm GaN layer on a p-type Si(111) substrate by metal organic chemical vapor deposition (see the wafer structure in Fig. S1(a) in the supplementary material), were obtained from DOWA Electronics Materials (Tokyo, Japan). The samples were first solvent cleaned in acetone, methanol, and isopropanol for one minute each. These samples were then immediately mounted to a sample plate and introduced into an ultra-high vacuum (UHV) system, described in detail elsewhere, which consists of a number of vacuum chambers interconnected by a UHV transfer tube, maintained at <5 × 10$^{-10}$ mbar. This configuration enables the study of in situ surface treatments, thin film depositions, and surface characterization without exposure to atmospheric conditions, preventing spurious surface contamination.

In order to monitor the growth and reaction of Al$_2$O$_3$ on the AlGaN surface, XPS was carried out after specific points in the study: (a) after loading the samples to UHV, (b) upon exposing the samples to an atomic layer deposition reactor (Picosun PR200 PEALD reactor (Masala, Finland) operated under purely thermal or plasma-enhanced modes for comparison) for 30 min of annealing (300 °C and 200 °C for ALD and PEALD, respectively, consistent with the following deposition temperature), and (c) after each individual “half cycle” pulse of the ALD/PEALD process up to two full cycles. Specifically, the samples were first exposed to one pulse of TMA in the reactor and interrogated with XPS, then transferred back to the PEALD reactor and exposed to one pulse of H$_2$O (ALD) or remote O$_2$ plasma (PEALD) prior to again being examined with XPS. The samples were also examined with XPS after 5, 10, 20, and 100 full cycles. In situ LEIS was also performed on the sample surface after 20 cycles.

In this study, one full thermal ALD sequence is 0.1 s TMA + 6 s Ar Purge + 0.1 s H$_2$O + 4 s Ar Purge, and the deposition temperature was 300 °C; one full PEALD cycle sequence is 0.1 s TMA + 6 s Ar purge + 28 s remote O$_2$ plasma + 4 s Ar purge, and the deposition temperature was 200 °C. The remote O$_2$ plasma was generated by 160 sccm O$_2$ flow at 2.75 kW. High purity (99.99999%) Ar was used as the precursor carrier and purging gas. The base pressure of the reactor was ~5 mbar.

The XPS was carried out using a monochromated Al k$_\alpha$ (h$\nu$ = 1486.7 eV) X-ray source, equipped with a 7 channel...
All peaks were referenced to the N 1s core level with respect to the sample normal. XPS peak deconvolution was carried out using an analyzer software with a detailed peak fitting procedure described elsewhere.\textsuperscript{14,33} All peaks were referenced to the N 1s peak at 397.0 eV to compensate for any shifts in the peak positions due to band bending. The LEIS was carried out using the same 7 channel analyzer with biasing conditions suitable for ion detection, and He\textsuperscript{+} ions excited by an ISE 100 fine focus ion gun using 1 kV bias and 10 mA emission current.

Additional $\sim 1 \times 1$ cm\textsuperscript{2} AlGaN samples from the same wafer were similarly prepared with subsequent 100 cycles of PEALD Al\textsubscript{2}O\textsubscript{3} (for a nominal Al\textsubscript{2}O\textsubscript{3} thickness of $\sim 10 \text{nm}$ verified by \textit{ex situ} ellipsometry carried on 100 cycles of Al\textsubscript{2}O\textsubscript{3} on Si reference samples) for device fabrication. The fabrication process is described in the supplementary material.\textsuperscript{30} The schematic diagrams and geometry details of MOS diodes and transistors are also depicted in Figs. S1(b) and S1(c) in the supplementary material, respectively.\textsuperscript{30} C-V measurements were performed on the diodes by an Agilent 4284 LCR meter with a step of 0.2 V and AC modulation voltage of 50 mV with sweep frequencies varying from 5 to 400 kHz. I-V measurements were carried out using a Keithley 4200. All C-V and I-V characterizations were performed in the dark to avoid the influence of photoionization of trapped electrons.\textsuperscript{34}

The N 1s and Ga LMM Auger spectra for each individual step are shown in Fig. 1(a). Ga/Al-N bonding (397.0 eV) and the Ga L\textsubscript{2,3}M\textsubscript{4,5}M\textsubscript{4,5} Auger feature (spanning $\sim 392–398$ eV) are detected. After 20 cycles of PEALD Al\textsubscript{2}O\textsubscript{3}, the intensities of N 1s and Ga LMM decrease by $\sim 65\%$ due to the attenuation of the overlying Al\textsubscript{2}O\textsubscript{3} film. In order to understand chemical states of nitrogen clearly, the N 1s and Ga LMM spectra after annealing and after 20 cycles of PEALD Al\textsubscript{2}O\textsubscript{3} are shown in Fig. 1(b). There is no evidence of detectable Ga-ON ($\sim 398$ eV) or N-O ($\sim 402$ eV) bonding, which results in undesirable defects on AlGaN according to our previous \textit{in situ} O\textsubscript{2} plasma pretreatment work.\textsuperscript{12} The N 1s/Ga LMM ratio decreases slightly after 20 cycles of Al\textsubscript{2}O\textsubscript{3} because of a formation of surface Ga/Al oxide, and will be further discussed in the Ga 2p\textsubscript{3/2} and Al 2p spectra below.

The C 1s spectra for each individual step are shown in Fig. 1(c). For the initial starting surface, C=O ($\sim 290$ eV) and C-(O)H/C-C ($\sim 284.5$ eV) bonds are detected. The \textit{in situ} 200$^\circ$C annealing is not effective at removing the carbon concentration, consistent with our previous work.\textsuperscript{14,32} In order to observe the initial reaction between the AlGaN surface and TMA/O\textsubscript{2} plasma, the C 1s spectra for the first two full ALD cycles (four half cycles) are also shown in Fig. 1(d). After the first pulse of TMA, the carbon concentration does not increase. Upon exposure to the first pulse of the O\textsubscript{2} plasma (28 s), the C 1s peaks, especially the C(O)/H-C-C concentration, decreases significantly while the intensity of the C=O feature does not change. After the second pulse of TMA, the C 1s peak at $\sim 284.5$ eV corresponding to Al-CH\textsubscript{3} binding clearly appears. This behavior indicates that the first pulse of O\textsubscript{2} plasma changes the AlGaN surface, which provides nucleation sites for the following TMA precursor. After the second pulse of O\textsubscript{2} plasma, the C 1s peaks corresponding to C-H bonds decrease again, suggesting the removal of CH\textsubscript{3} and a full cycle of TMA/O\textsubscript{2} plasma reaction. The carbon concentration after 20 cycles of PEALD is below XPS detection limits, suggesting a complete reaction with minimized carbon incorporation.

Fig. 2(a) presents the normalized and deconvoluted Ga 2p\textsubscript{3/2} spectra for each individual deposition stage, and shows two peaks indicative of Ga-N bonding from the substrate and Ga-O bonding at the surface. In our work, Ga 2p\textsubscript{3/2} spectra are commonly used due to the superior surface sensitivity (and signal intensity) of the Ga 2p\textsubscript{3/2} spectra relative to other Ga spectral peaks produced using the Al K\textsubscript{\alpha} ($h\nu = 1486.7$ eV) source.\textsuperscript{35} The fitting parameters are consistent with our previous reports.\textsuperscript{10,12,14,18,32} The ratio of the Ga-O to Ga-N peak area (intensity) for the PEALD Al\textsubscript{2}O\textsubscript{3} is plotted in Fig. 2(b). As a reference, the ratio of the Ga-O/Ga-N peak areas for the ALD Al\textsubscript{2}O\textsubscript{3} is also plotted in Fig. 2(b). The first pulse of TMA does not change the Ga-O concentration. An obvious increase of Ga-oxide is detected after the first pulse of O\textsubscript{2} plasma, but not after the first H\textsubscript{2}O precursor as shown in Fig. 2(b). This indicates that the remote plasma oxygen...
exposure oxidizes the AlGaN surface. Upon exposure to the second pulse of TMA, the Ga-O peak decrease is likely due to the formation Ga-O-Al bonding at the surface.\(^{10}\) The final Ga-O/Ga-N intensity ratios are \(\sim11.7 \pm 1.5\%\) and \(16.9 \pm 1.9\%\) for ALD and PEALD Al\(_2\)O\(_3\), respectively. If we assume that the surface oxide layer consists of \(75\%\) Ga\(_2\)O\(_3\) and \(25\%\) Al\(_2\)O\(_3\), the thickness of the Ga/Al oxide layers after 20 cycles of ALD Al\(_2\)O\(_3\) and PEALD are both less than 0.1 nm based on the intensity attenuation of the N 1s peak, which is below the monolayer (\(\sim0.26\) nm) coverage. In summary, the PEALD process slightly increases the oxide concentration at the surface relative to the ALD process.

The Al 2p spectra for each individual stage in PEALD are shown in Fig. 3(a), which is a direct monitor of the growth of Al\(_2\)O\(_3\). The ratio of Al-O to Al-N during the half cycle PEALD is shown in Fig. 3(b) and the ratio of the Al-O/Al-N for each stage during ALD of Al\(_2\)O\(_3\) is also shown. The detection of the Al-N bulk peak at 73.5 eV, as well as Al\(_2\)O\(_3\) at 74.4 eV, is noted.\(^{14,32}\) Due to the low binding energy of Al 2p core level, the intensity of Al-O bond from the substrate is less prominent compared to the detection of Ga-O from the surface sensitive Ga 2p\(_{3/2}\) core level.\(^{4,10,12,14,18,32}\) Consistent with Ga 2p\(_{3/2}\) spectra, the Al-O bond increases slightly after annealing and the first pulse of O\(_2\) plasma. Importantly, the intensity ratio for PEALD increases faster than the ALD process, indicating the nucleation or growth of PEALD Al\(_2\)O\(_3\) on AlGaN is more facile than ALD. It should be noted that measured Al\(_2\)O\(_3\) growth rates on Si substrate for ALD and PEALD are 1.14 \pm 0.01 and 1.13 \pm 0.01 Å/cycle, respectively, suggesting that the difference of growth rates could be ignored here. The thickness of the PEALD Al\(_2\)O\(_3\) after 20 cycles on AlGaN is \(\sim1.4\) nm according to the attenuation of Ga 2p\(_{3/2}\) peak area. In contrast, the thickness of ALD Al\(_2\)O\(_3\) is \(\sim1.0\) nm after 20 cycles. Thus, the relatively enhanced growth is due to Ga/Al-oxide formation (which are reactive nucleation sites for the TMA precursor) after the O\(_2\) plasma exposure, likely coupled with the removal of carbon contamination, which may mitigate the reaction between the AlGaN surface and the TMA precursor.\(^{10}\) Additionally, a much better coverage of Al\(_2\)O\(_3\) by PEALD is demonstrated by \textit{in situ} LEIS, which is sensitive to only the outmost exposed atomic layers on the surface.\(^{36}\) As Fig. 3(c) shows, no Ga peak is detected while an obvious Ga peak (815 eV) is found with 20 cycles of ALD Al\(_2\)O\(_3\) on AlGaN, suggesting that the PEALD Al\(_2\)O\(_3\) results in the complete coverage at the initial stage. Moreover, the higher Al peak from the ALD Al\(_2\)O\(_3\) sample relative to the PEALD Al\(_2\)O\(_3\) is also due to the uncovered AlGaN surface. The stoichiometry of the ALD Al\(_2\)O\(_3\) and the PEALD is the same within detectable limits (see Fig. S2 in the supplementary material\(^{10}\)). The detection of a small fluorescent (F) peak is noted and is due to decomposition of reactor elastomer seals. The concentration of F is below XPS detection limits and does not affect the discussion here.

The frequency-dependent C-V curves from 5 kHz to 400 kHz at room temperature are measured to evaluate the interface quality. These C-V curves from diode structures incorporating ALD Al\(_2\)O\(_3\) and PEALD Al\(_2\)O\(_3\) dielectric layers are shown in Figs. 4(a) and 4(b), and reveal a standard two-step C-V feature.\(^{12,18}\) Capacitance values for diodes at the plateau where the two dimension electron gas (2DEG) forms are 194 and 196 nF/cm\(^2\) for ALD and PEALD, respectively, consistent with the \(\sim10\) nm Al\(_2\)O\(_3\)/AlGaN stack capacitance.\(^{4}\) Obvious frequency dependence of capacitance dispersion is detected for both diodes upon further gate bias, corresponding to a high \(D_{it}\). Here, “border trap” (trap states inside the gate insulator but close to the interface) should not be key sources of the \(D_{it}\) at the Al\(_2\)O\(_3)/AlGaN interface. Our previous work demonstrates that Al\(_2\)O\(_3)/AlGaN and HfO\(_2)/AlGaN diodes present a similar level of \(D_{it}\), and AlGaN surfaces have a much more impact on the \(D_{it}\). Long \textit{et al.} also show the absence of border traps for ALD Al\(_2\)O\(_3)/AlGaN interface.\(^{37}\) The PEALD approach decreases the dispersion slightly. This may be due to the formation of Ga-O, which likely passivates the AlGaN surface.\(^{18}\) The forward and backward C-V curves at 100 kHz can be seen as insets within Figs. 4(a) and 4(b), and show very small hysteresis values (\(\Delta V\)):0.09 and 0.13 V for ALD and PEALD Al\(_2\)O\(_3\), respectively. It is thought that the PEALD process does not contribute a significant density of slow traps.\(^{12}\) The gate leakage current densities of Schottky AlGaN/GaN, ALD Al\(_2\)O\(_3)/AlGaN/GaN, and PEALD Al\(_2\)O\(_3)/AlGaN/GaN are shown in

FIG. 3. (a) \textit{In situ} XPS spectra of Al 2p core levels from initial surface, after annealing in 200 °C, and each individual ALD half cycle. (b) The ratio of Al-O/Al-N from Al 2p peaks during half cycle ALD and PEALD indicating the growth of Al\(_2\)O\(_3\) on AlGaN. (c) Comparison of LEIS after 20 cycles of ALD to the PEALD Al\(_2\)O\(_3\) studied here. (See 25 cycles of ALD Al\(_2\)O\(_3\) on AlGaN in Ref. 10.)

FIG. 4. Comparison of frequency-dependent C-V curves for (a) ALD Al\(_2\)O\(_3)/AlGaN/GaN and (b) PEALD Al\(_2\)O\(_3)/AlGaN/GaN diodes. Insets show forward and backward C-V curves. (c) Leakage current density-voltage plots for Schottky AlGaN/GaN, ALD Al\(_2\)O\(_3)/AlGaN/GaN, and PEALD Al\(_2\)O\(_3)/AlGaN/GaN diodes.
Fig. 4(c). Either ALD or PEALD Al2O3 layer effectively suppresses the leakage current, consistent with the relatively high conduction band offset (CBO) values in the band diagram (see Figs. S3(c) and S3(f))\textsuperscript{(30)}. It should be noted that the O2 plasma in the PEALD is well controlled using a relative short exposure time (28 s/per pulse) and a low substrate temperature (200°C). In contrast, our previous work shows that a 10 min of 300°C O2 plasma excited by another RF plasma generator results in a worse frequency dispersion than ALD Al2O3/AlGaN/GaN diodes.\textsuperscript{(18)} Therefore, it is essential to control and optimize the O2 plasma conditions for a specific tool carefully.

The threshold voltage ($V_{TH}$) values extracted from $I_D$-$V_D$ curves are $-3.9$, $-10.3$, and $-9.5$ V for HEMTs, ALD-MOSHEMTs, and PEALD-MOSHEMTs, respectively, and the extrapolation methods are included in supplementary material.\textsuperscript{(30)} Obviously, a negative $V_{TH}$ shift is detected from previous studies, the formation Ga-O-N, but not Ga-O, is a sign of device degradation.\textsuperscript{(12,18)} The Al/Ga-oxide passivates the AlGaN surface and decreases $D_{it}$ as well as the OFF-state leakage. As expected, the PEALD Al2O3 layer reduces the gate leakage current, similar to ALD Al2O3. Overall, PEALD Al2O3 is an appropriate technology for the Al2O3 growth on AlGaN.

This work was supported by the Asian Office of Aerospace Research and Development (AOARD) through the Air Force office of Scientific Research (AFOSR) under Grant No. FA2386-14-1-4069. The authors thank Dr. J. Kim, Dr. Y. Byun, and Mr. A. Lucero for helpful discussions.

30See supplementary material at http://dx.doi.org/10.1063/1.4929818 for additional device fabrication, band diagrams and the extraction of threshold voltage.
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