In-situ X-ray photoelectron spectroscopy of trimethyl aluminum and water half-cycle treatments on HF-treated and O₃-oxidized GaN substrates

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We have investigated the effect of trimethyl aluminum (TMA) and water (H₂O) half-cycle treatments on HF-treated, and O₃-oxidized GaN surfaces at 300 °C. The in-situ X-ray photoelectron spectroscopy results indicate no significant regrowth of Ga–O–N or self-cleaning on HF-treated and O₃-oxidized GaN substrates with exposure to water and TMA. This result is different from the self-cleaning effect of Ga₂O₃ seen on sulfur-treated GaAs or InGaAs substrates. O₃ causes aggressive oxidation of GaN substrate and direct O–N bonding compared to H₂O.

1 Introduction GaN (Group-III nitride) technology has been widely used in optoelectronics, radio frequency (RF) transistors, and power switching due to a suitable band gap, excellent transport properties, high breakdown field, low power losses, as well as the possibility of forming a heterojunction structure on low cost, large area substrate templates such as Si, sapphire, etc. [1, 2]. The introduction of a high-quality, ultrathin, atomic layer deposited (ALD) dielectric between the metal and semiconductor has been shown to effectively decrease diode leakage current without compromising Metal Oxide Semiconductor-High Electron Mobility Transistor (MOS-HEMT) transfer characteristics [3–5]. The evaluation of the role of native oxides as well as ALD dielectric films along with their interaction with the underlying substrate could provide valuable information for device applications [6]. Therefore, in this work, we have investigated the growth of ALD Al₂O₃ on top of HF-treated and O₃-oxidized, n-type GaN.

2 Methods 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/H₂O for 2 min each), wet chemical cleaning (2% HF for 2 min followed by 2 min H₂O rinse) and blown dry with N₂ [7, 8]. Immediately after surface preparation, the samples were loaded in an ultra high vacuum (UHV) custom tool with an integrated monochromatic Al Kα XPS (hv = 1486.7 eV) and an SUNALE® ALD reactor as described in detail elsewhere [8–11]. TMA from SAFC Hi-tech® was used as the metal precursor. H₂O (de-ionized water with a resistivity of ~18 MΩ) vapor was used as the oxidant. O₃ 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. Ultrahigh purity nitrogen (N₂, 99.999%) was used as the purge gas. The TMA- and H₂O-injection pulse times were both 1s, respectively. In-situ XPS was obtained after each TMA or H₂O half-cycle reaction on the HF-treated and O₃-oxidized GaN. The XPS data was charge referenced to the N 1s (397.9 eV) core level from the GaN substrate [12].
3 Results and discussion  Both as-received and HF-treated GaN substrates showed carbon and oxygen on the surface, and the presence O–C bonding (such as C–O–H, C–O–R at ~286 eV, and C–O–O–R, –CO3 at ~288 eV). As expected, the concentrations of surface C and O are lowered after the HF-treatment, however, complete removal was not possible (not shown here). After HF treatment, the atomic% of C decreased from 18.6% to 4.0% and atomic% of O decreased from 14.6% to 6.8%. O3 oxidation of HF-cleaned GaN caused a ~5x increase in O 1s peak area indicating O incorporation in the GaN substrate. C was close to the XPS detection limit. The corresponding cross-sectional high resolution transmission electron microscopy images of HF-cleaned and O3 treated GaN are shown in Fig. 1. An approximately 1.5–2 nm thick lighter contrast layer was seen for the O2-oxidized GaN substrate indicative of GaO(N) growth at the GaN surface.

Figure 1c shows the normalized Ga 2p3/2 XPS for HF-treated and O3-oxidized GaN substrates. The area under the Ga 2p3/2 peak for HF-treated GaN is shaded for comparison with the O2-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 [13, 14]. Although the low oxidation temperature of 400 °C should not substantially oxidize GaN [13, 14], the presence of O3 as the oxidant is expected to cause aggressive oxidation of GaN. The 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 O2 half-cycle during AID Al2O3 growth [15]. 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) [10, 11] 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 2a shows the normalized Ga 2p3/2 in-situ XPS data for TMA/H2O half-cycle study on HF-treated GaN. The Ga 2p3/2 after HF-treatment, vacuum anneal for 10 minutes at 300 °C (ALD bake), 1st TMA, 1st H2O, 15th TMA, 15th H2O, and 30th H2O half-cycle reactions are shown. There is no noticeable peak broadening after the TMA/H2O half-cycle studies up to the 30th H2O half-cycle reaction. This is indicative of no substantial growth of Ga–O–X on HF-treated GaN surface during the AID Al2O3 growth at 300 °C and highlights the extreme oxidation resistance of GaN. Figure 2b shows the normalized Ga 2p3/2 in-situ XPS data for TMA/H2O half-cycle treatments on O3-oxidized GaN. The Ga 2p3/2 peak remains nearly identical in FWHM after the subsequent 1st TMA and 1st H2O half-cycles on O3-oxidized GaN. The corresponding O 1s data is shown as insets both for HF-treated GaN (Fig. 2a, inset) and O3-oxidized GaN (Fig. 2b, inset). For HF-treated GaN, the ALD growth causes an increase in O 1s peak area as a function of the ALD cycle. In the case of O3-oxidized GaN, the O 1s data indicates no significant change in the peak area after the 1st TMA and 1st H2O half-cycles. These Ga 2p3/2 in-situ XPS results imply that the TMA/H2O half-cycle reactions on HF-treated and O3-oxidized GaN do not cause either substantial growth or self-cleaning of GaO(N) components. This result is in contrast to the self-cleaning of Ga2O3 on sulfur-treated GaAs and InGaAs substrates at similar deposition temperatures [9, 10, 15, 16].

Figure 3 shows the N 1s and Al 2p data for HF-treated and O3-oxidized GaN substrates. The N 1s XPS region
overlaps with Ga(LMM) Auger lines at the lower binding energy range of 390–395 eV. The N 1s peak corresponding to N–Ga substrate peak appears at ≈397.9 eV and N–O bonding appears at ≈402–407 eV [12]. For HF-treated GaN in Fig. 3, the N 1s XPS is shown prior to ALD and to N–Ga bonding along with Ga Auger lines. However, there is no clear N–O peak in either case. This result was also true for the initial ALD cycles starting from HF-treated GaN surface. For O3-oxidized GaN, there is an N–O peak at ≈403 eV in addition to the N–Ga substrate peak. This result shows that nitrogen is directly bonded to oxygen (N–O) when O3 is used for substrate oxidation, whereas no such bonding is seen when H2O is used as the oxidant. After the 1st TMA/H2O half-cycle treatment, the N–O bonding is still seen showing no significant self-cleaning of the N–O component during Al2O3 deposition.

The Al 2p photoelectron lines for HF-treated GaN (baseline), HF-treated GaN with a subsequent single cycle of TMA, and O3-treated GaN also with a subsequent single cycle of TMA were studied (Fig. 3b). There is no Al detected for the baseline substrate. When HF-treated GaN is exposed to the 1st TMA pulse, a very low intensity of Al 2p is seen, close to the detection limits of XPS. However, in the case of O3-oxidized GaN, a much higher intensity Al 2p peak is seen. It is evident that the O3-oxidized GaN surface provides better nucleation sites for ALD Al2O3 compared to HF-treated GaN. Therefore, the incubation time for ALD Al2O3 growth on O3-oxidized GaN is expected to be shorter. The nucleation of the Al2O3 dielectric would depend on the number of reactive sites (–OH groups) available for the ligand exchange mechanism with TMA [17]. Further studies of the ligand exchange mechanisms are needed to understand the facile ALD Al2O3 nucleation on oxidized GaN surfaces.

4 Summary We have investigated TMA/H2O half-cycle treatments on HF-treated and O3-oxidized GaN surfaces at 300 °C. The in-situ XPS results indicate no significant self-cleaning effect or growth of Ga–O–N on the GaN substrate during ALD. O3 exposure causes aggressive oxidation of the GaN substrate and direct N–O bonding compared to H2O exposure. The incubation time for Al2O3 growth on oxidized GaN is shorter compared to that on HF-treated GaN.

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