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 (H_2O) 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 Ga_2O_3 seen on sulfur-treated GaAs or InGaAs substrates. O₃ causes aggressive oxidation of GaN substrate and direct O–N bonding compared to H_2O.

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 Al_2O_3 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 sub-strate. 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 [7, 8]. Immediately after surface preparation, the samples were loaded in an ultra high vacuum (UHV) custom tool with an integrated monochromatic Al K_α 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. H_2O (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 (N_2, 99.999%) was used as the purge gas. 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 O₃-oxidized GaN. The XPS data was charge referenced to the N 1s (397.9 eV) core level from the GaN substrate [12].

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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, –CO_3 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%. O_3 oxidation of HF-cleaned GaN caused a ∼5× 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 O_3 treated GaN are shown in Fig. 1. An approximately 1.5–2 nm thick lighter contrast layer was seen for the O_3-oxidized GaN substrate indicative of GaO(N) growth at the GaN surface.

Figure 1c shows the normalized Ga $2p_{3/2}$ XPS for HF-treated and O_3-oxidized GaN substrates. The area under the Ga $2p_{3/2}$ peak for HF-treated GaN is shaded for comparison with the O_3-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 O_3-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 O_3-oxidation [13, 14]. Although the low oxidation temperature of 400 °C should not substantially oxidize GaN [13, 14], the presence of O_3 as the oxidant is expected to cause aggressive oxidation of GaN. The aggressive oxidation by O_3 was previously shown by Brennan et al. where O_3 caused formation of thicker Ga-oxides on InGaAs even after the 1st O_3 half-cycle during AlD Al_2O_3 growth [15]. Figure 1(inset) shows the O 1s raw data
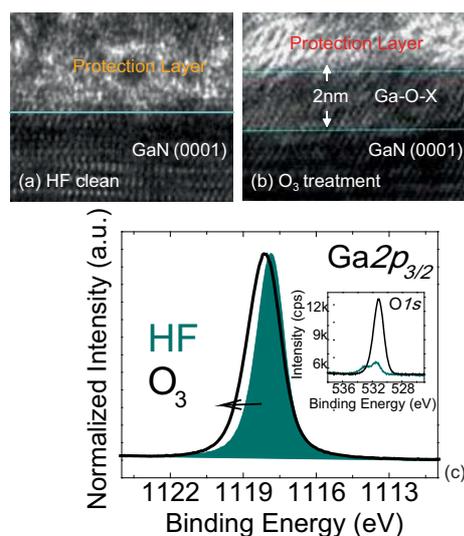
Figure 1 (online colour at: www.pss-rapid.com) TEM images of (a) HF-cleaned and (b) O_3-treated GaN are shown. Part (c) shows the Ga $2p_{3/2}$ XPS of HF-treated and O_3-oxidized GaN. The inset figure shows the O1s data for the corresponding samples.
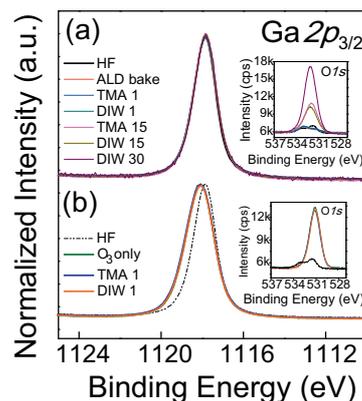
Figure 2 (online colour at: www.pss-rapid.com) (a) Ga $2p_{3/2}$ in situ XPS on HF-treated GaN including HF-treatment, ALD bake, and TMA/DIW half-cycle study for up to 30 ALD cycles. (b) Ga $2p_{3/2}$ in situ XPS on O_3-oxidized GaN before and after TMA/DIW half-cycle treatments. The O 1s data is shown as insets both for HF-treated GaN (Fig. 2a, inset) and O_3-oxidized GaN (Fig. 2b, inset).

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 O_3-oxidized GaN.

Figure 2a shows the normalized Ga $2p_{3/2}$ in-situ XPS data for TMA/H_2O half-cycle study on HF-treated GaN. The Ga $2p_{3/2}$ after HF-treatment, vacuum anneal for 10 minutes at 300 °C (ALD bake), 1st TMA, 1st H_2O, 15th TMA, 15th H_2O, and 30th H_2O half-cycle reactions are shown. There is no noticeable peak broadening after the TMA/H_2O half-cycle studies up to the 30th H_2O half-cycle reaction. This is indicative of no substantial growth of Ga–O–X on HF-treated GaN surface during the ALD Al_2O_3 growth at 300 °C and highlights the extreme oxidation resistance of GaN. Figure 2b shows the normalized Ga $2p_{3/2}$ in-situ XPS data for TMA/H_2O half-cycle treatments on O_3-oxidized GaN. The Ga $2p_{3/2}$ peak remains nearly identical in FWHM after the subsequent 1st TMA and 1st H_2O half-cycles on O_3-oxidized GaN. The corresponding O 1s data is shown as insets both for HF-treated GaN (Fig. 2a, inset) and O_3-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 O_3-oxidized GaN, the O 1s data indicates no significant change in the peak area after the 1st TMA and 1st H_2O half-cycles. These Ga $2p_{3/2}$ in-situ XPS results imply that the TMA/H_2O half-cycle reactions on HF-treated and O_3-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 Ga_2O_3 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 O_3-oxidized GaN substrates. The N 1s XPS region
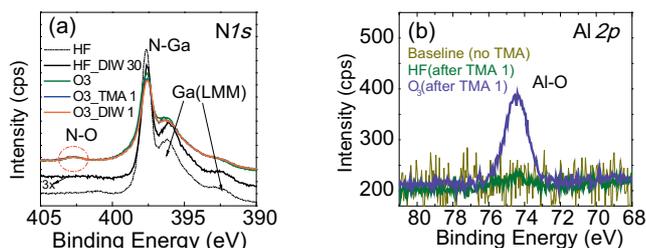
Figure 3 (online colour at: www.pss-rapid.com) (a) N 1s XPS of HF-treated and O_3-oxidized GaN are shown. (b) Al 2p in situ XPS is shown.

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 after the 30th H_2O ALD half-cycle. There is 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 O_3-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 O_3 is used for substrate oxidation, whereas no such bonding is seen when H_2O is used as the oxidant. After the 1st TMA/H_2O half-cycle treatment, the N–O bonding is still seen showing no significant self-cleaning of the N–O component during Al_2O_3 deposition.

The Al 2p photoelectron lines for HF-treated GaN (baseline), HF-treated GaN with a subsequent single cycle of TMA, and O_3-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 O_3-oxidized GaN, a much higher intensity Al 2p peak is seen. It is evident that the O_3-oxidized GaN surface provides better nucleation sites for ALD Al_2O_3 compared to HF-treated GaN. Therefore, the incubation time for ALD Al_2O_3 growth on O_3-oxidized GaN is expected to be shorter. The nucleation of the Al_2O_3 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 Al_2O_3 nucleation on oxidized GaN surfaces.

4 Summary We have investigated TMA/H_2O half-cycle treatments on HF-treated and O_3-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. O_3 exposure causes aggressive oxidation of the GaN substrate and direct N–O bonding compared to H_2O exposure. The incubation time for Al_2O_3 growth on oxidized GaN is shorter compared to that on HF-treated GaN.

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