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Interfacial chemistry and valence band offset between GaN and Al₂O₃ studied by X-ray photoelectron spectroscopy

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The interface region between Ga-face n-type GaN and Al₂O₃ dielectric (achieved via atomic-layer deposition or ALD) is investigated by X-ray photoelectron spectroscopy (XPS). An increase in the Ga-O to Ga-N bond intensity ratio following Al₂O₃ deposition implies that the growth of an interfacial gallium sub-oxide (GaO_x) layer occurred during the ALD process. This finding may be ascribed to GaN oxidation, which may still happen following the reduction of a thin native GaO_x by trimethylaluminum (TMA) in the initial TMA-only cycles. The valence band offset between GaN and Al₂O₃, obtained using both core-level and valence band spectra, is found to vary with the thickness of the deposited Al₂O₃. This observation may be explained by an upward energy band bending at the GaN surface (due to the spontaneous polarization induced negative bound charge on the Ga-face GaN) and the intrinsic limitation of the XPS method for band offset determination.

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The performance of conventional GaN-based high electron-mobility transistors (HEMTs) is limited by the intrinsically high leakage current of the Schottky gate.^{1–4} Moreover, it is known that GaN reacts with oxygen even at room temperature to form a layer of gallium sub-oxide (GaO_x) on the surface.^{5–8} Defect states associated with the GaO_x further exacerbate gate leakage and cause drain-current collapse at high frequency.^{1,9–11} Recently, it was shown that the adoption of a high-permittivity metal oxide as the gate insulator and surface passivation layer in metal-insulator-semiconductor HEMTs (MIS-HEMTs) could help mitigate the above issues.^{4,12–14} MIS-HEMTs, which combine the merits of HEMT and the MIS device, are deemed the most promising next-generation high-power electronic devices.

Al₂O₃ is a popular choice for the gate insulator by virtue of its high band gap energy ($E_g \sim 7\text{--}9\text{ eV}$), dielectric constant ($\epsilon \sim 9$), and breakdown field ($E_{bd} \sim 10\text{ MV/cm}$). In addition, Al₂O₃ has a more negative Gibbs free energy (-1582 kJ/mol) as compared to Ga₂O₃ (-998 kJ/mol),¹⁵ indicating that it may be possible for GaO_x to be converted into Al₂O₃ to improve the interface quality. Studies on the atomic-layer deposition (ALD) of Al₂O₃ on GaAs have indeed shown the reduction of native oxide by the trimethyl-aluminum (TMA) precursor.^{16,17} However, there are few studies on the ALD of Al₂O₃ on GaN, especially in regard to the electronic structure of the GaN/Al₂O₃ interface. Thus, a systematic study of GaN surface passivation by Al₂O₃ is of utmost practical importance.

The test samples were fabricated on GaN-on-Si(111) substrates purchased from a commercial company. A transition layer separates the Si substrate from the Ga-terminated GaN epilayers, which comprise a $1\text{ }\mu\text{m}$ Si-doped GaN layer on top of a $0.2\text{ }\mu\text{m}$ intrinsic GaN layer. The Ga-face wafer was chosen in our study because of its smooth surface

morphology and high material quality,¹⁸ making it a preferred choice for device applications. The wafers were initially degreased for 5 min in acetone and subsequently in isopropyl alcohol. The native oxide was etched by a dip in a diluted hydrofluoric acid solution (HF:H₂O = 1:20) for $\sim 3\text{ min}$, followed by a rinse in flowing de-ionized water. Al₂O₃ was deposited by ALD, with TMA and H₂O as the metal precursor and oxidant, respectively. The chamber temperature was held at $250\text{ }^\circ\text{C}$ during deposition. The Al₂O₃ deposition started off with two TMA pulses, aimed at reducing the native oxide layer.^{16,17} This was followed by regular deposition cycles consisting of a TMA pulse and then a H₂O pulse. The Al₂O₃ thickness was measured using a VB-250 Spectroscopic Ellipsometer. Samples with 0, 1.3, and 4 nm thick Al₂O₃ were fabricated and they are denoted as S1, S2, and S3, respectively, in the following discussion. To check the impact of the TMA and H₂O pulse sequence, another set of samples S4 and S5 each having a 4 nm Al₂O₃ was prepared without the initial two TMA pulses. The Al₂O₃ in S4 was deposited with H₂O pulse first followed by TMA pulse while that in S5 was deposited with TMA pulse first and then H₂O pulse. XPS measurements were carried out using a monochromatic Al K α X-ray source of energy 1486.7 eV. The XPS spectra reported here are referenced to the C 1s peak at the binding energy (BE) of 285.0 eV and the spectra are curve-fitted with a combination of Gaussian and Lorentzian line shapes, using a Shirley-type background subtraction.

The Ga 3d core-level spectra for S1–S3 are depicted in Fig. 1(a). Each Ga 3d spectrum could be deconvoluted into two components, corresponding to the Ga-N and Ga-O bonds. Existence of the Ga-O spectrum in S1 (without Al₂O₃ deposition) may be attributed to the inevitable reoxidation of the GaN surface after cleaning. The ratio of the Ga-O to Ga-N peak for this sample is 0.15. This ratio is 0.24 for S2 (1.3 nm Al₂O₃), implying that the growth of GaO_x occurred

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FIG. 1. The XPS Ga 3d core-level spectra for (a) S1-S3 and (b) S4 and S5.

during Al₂O₃ deposition. For S3 (4 nm Al₂O₃), however, the Ga-O/Ga-N ratio of 0.26 is not significantly different from that of S2. This implies that the GaO_x growth occurs mainly during the initial ALD cycles and it saturates after a thicker Al₂O₃ is deposited. Fig. 1(b) shows the Ga 3d spectra and the corresponding Ga-N and Ga-O components for S4 and S5. The Ga-O to Ga-N peak ratios of 0.22 and 0.23 for S4 and S5, respectively, are comparable and similar to those for S2 and S3, indicating that the sequence of the TMA and H₂O pulses has no apparent impact on the growth of GaO_x during Al₂O₃ deposition.

Reduction of the native oxide by TMA was observed during ALD of Al₂O₃ on GaAs.^{16,17} In our case, however, the growth of GaO_x is observed during ALD of Al₂O₃ on GaN. The difference may be explained. In Refs. 16 and 17, Al₂O₃ deposition was made either directly on a wafer removed from a sealed holder¹⁶ or after pre-heating at 320 °C for 30 min.¹⁷ The native oxide was relatively thick and its subsequent interaction with the initial TMA-only cycles might have led to part of it being converted into Al₂O₃. In our case, however, the native oxide was thinner because (1) the wafer was dipped in HF before it was loaded into the ALD chamber for Al₂O₃ deposition; (2) the wafer stage was pre-heated to the deposition temperature to enable the ALD process to begin soon after the wafer was loaded. Although the regrowth of GaO_x before the start of the ALD process was inevitable due to the high temperature, it could not explain the similar Ga-O/Ga-N bond ratio of S2-S5. In S2 and S3, since TMA-only cycles were initially applied, part of the regrown native oxide would have been converted

into Al₂O₃ and thus the Ga-O/Ga-N bond ratio should be lower than those for S4 and S5. Instead, comparable Ga-O/Ga-N bond ratios are obtained, implying that the extent of GaO_x growth was similar in all samples regardless whether TMA-only cycles were used initially (S2 and S3) or the TMA and H₂O pulses were reversed (S4 and S5). We believe that after the TMA-only cycles, the resultant Al₂O₃ layer in S2 and S3 might be too thin (due to the initially thin native oxide) to prevent the oxidation of GaN in subsequent deposition cycles involving the H₂O pulse. Parasitic oxidation of GaN during plasma-assisted SiO₂ deposition was observed and was believed to have been caused by O species diffusing through the initially thin SiO₂ layer.⁷ We reckon that there should be a lower limit to the thickness of the native oxide so that the Al₂O₃ formed via the initial TMA-only cycles is sufficiently thick to suppress the growth of GaO_x during subsequent Al₂O₃ deposition. At the same time, the native oxide should be thin enough so that it could be fully converted into Al₂O₃ by the TMA-only cycles.

It is interesting to point out that the BE of the Ga 3d peak is shifted progressively towards smaller values as the Al₂O₃ thickness is increased (Fig. 1(a)). A similar observation applies to the N 1s spectra shown in Fig. 2(a). No difference is, however, seen in the Al 2p spectra for S2 and S3 (Fig. 2(b)). For both cases, only a single peak with a BE of ~74.3 eV, similar to that for the Al-O bond in bulk Al₂O₃, is evident. Table I summarizes the BEs of the Ga 3d, N 1s, and Al 2p peaks for S1-S3.

FIG. 2. (a) The XPS N 1s core-level spectra for S1-S3. (b) The XPS Al 2p core-level spectra for S2 and S3.

TABLE I. Summary of the binding energy of the intensity peak(s) in the Ga 3*d*, N 1*s* and Al 2*p* spectra as well as the GaN/Al₂O₃ valence band offset (VBO) for S2 and S3.

Sample No.	Al ₂ O ₃ thickness (nm)	Binding Energy (eV)					VBO (Ga 3 <i>d</i>)
		Ga 3 <i>d</i>			N 1 <i>s</i>	Al 2 <i>p</i>	
		GaN	Ga-O	GaO/GaN		Al-O	
S1	0.0	19.7	20.5	0.15	397.3	...	...
S2	1.3	19.4	20.1	0.24	397.1	74.3	0.7
S3	4.0	19.3	19.9	0.26	397.0	74.4	0.9

The nearly identical Al 2*p* spectra of S2 and S3 implies that the reduction in the BE of the Ga 3*d* and N 1*s* peaks are not related to the bulk property of the deposited Al₂O₃. A possible reason for the observed BE shifts is dipole formation at the GaN/Al₂O₃ interface. However, interface-dipole induced BE shift should saturate after the deposition of several monolayers of Al₂O₃ and may not adequately explain the continuous reduction of BE seen with the increase in Al₂O₃ thickness. To probe this further, the valence band offset (VBO) between Al₂O₃ and GaN is determined using the method first proposed by Kraut *et al.*¹⁹ as summarized in the following equation:

$$\text{VBO} = [E_{\text{CL}}^{\text{Al}_2\text{O}_3}(\text{b}) - E_{\text{V}}^{\text{Al}_2\text{O}_3}(\text{b})] - [E_{\text{CL}}^{\text{GaN}}(\text{b}) - E_{\text{V}}^{\text{GaN}}(\text{b})] - [E_{\text{CL}}^{\text{Al}_2\text{O}_3}(\text{i}) - E_{\text{CL}}^{\text{GaN}}(\text{i})]. \quad (1)$$

The subscript CL and V denote the BE for the “core-level” and “valence band maximum (VBM),” respectively. The bulk and interface BEs are represented, respectively, by the notation (b) and (i). The BE difference between core-level and VBM of bulk Al₂O₃ and GaN, which corresponds to the first and second square-bracket terms in Eq. (1), are given in Fig. 3. The VBM of each sample is determined by extrapolating the leading edge of the valence band spectrum to the base line (the cross-over points in Fig. 3).²⁰ Using the BE for the Al 2*p* and Ga 3*d* spectra as the core-level BE of bulk Al₂O₃ and GaN, respectively, the corresponding BE difference between the core-level and VBM are determined as 71.8 eV and 17.6 eV, as shown in Fig. 3. The value for the last square-bracket term in Eq. (1) is obtained from the difference in the core-level BE for Al 2*p* and Ga 3*d* (Table I). The value is 54.9 eV (=74.3 – 19.4) for S2 and 55.1 eV (=74.4 – 19.3) for S3. Therefore, the VBO between Al₂O₃ and GaN are 0.7 eV (=71.8 – 17.6 – 54.9) and 0.9 eV (=71.8 – 17.6 – 55.1) for S2 and S3, respectively.

It should be mentioned that since S2 and S3 were fabricated under identical conditions, the GaN/Al₂O₃ interface and hence, the VBO should be similar for both samples. This is supported by the identical VBO's (=0.9 eV) for S4 and S5, which were also fabricated under the same conditions. A possible explanation for the difference in the VBO's of S2 and S3 is given as follows. It is known that spontaneous polarization in GaN results in a surface bound charge, which is negative in the case of the Ga-face GaN.^{21–24} As a consequence, a compensating space charge comprising positive donors is formed near the GaN surface.^{5,9,25,26} The impact of

this positive space charge on XPS measurement of the Ga 3*d* electrons from samples having different Al₂O₃ thicknesses is depicted by the schematic diagrams in Figs. 4(a)–4(c). It should be noted that the Fermi level E_f in GaN serves as the reference energy level (0 eV) for XPS measurement. Because the negative surface bound charge depletes the n-type GaN, an upward bending of the energy bands occurs near the surface^{23,27} (Fig. 4(b)). Thus, the difference between E_f and the core level (as well as the VBM) in GaN decreases towards the surface. Since the X-ray penetration depth for a given energy remains approximately constant, the probe

FIG. 3. The Al 2*p* (a) and Ga 3*d* (b) core-level and valence band spectra for bulk Al₂O₃ (deposited by ALD) and GaN. The square and circle symbols represent the core-level and valence band spectra, respectively. The VBM is extrapolated from the intersection point between the leading edge of the valence band spectrum and the base line.

FIG. 4. (a) Schematic cross-sectional diagrams showing GaN without and with deposited Al₂O₃ of different thicknesses. (b) Corresponding schematic energy band alignment diagrams for the cross-sectional diagrams in (a). The XPS binding energy for the Ga 3d and Al 2p core levels are measured with respect to the Fermi level E_F . (c) A schematic diagram showing the effect of the upward surface band bending in GaN on VBO determination using XPS.

depth in the GaN layer in S3 having a thicker Al₂O₃ is shallower than that in S2 (Fig. 4(c)). Thus, the GaN photoelectrons sensed during XPS measurement of S3 comes mainly from nearer the surface region where the difference between E_F and the core level (and VBM) is smaller. Hence, the resultant XPS spectra, which are determined from the weighted average of photoelectrons emitted from a certain depth in the sample, are shifted towards smaller energies, and the extracted VBO₃ is larger, as compared to those of S2 (Fig. 4(c)). To further confirm the effect of the upward surface band bending in GaN on the VBO between GaN and Al₂O₃, the VBM difference between bulk Al₂O₃ and GaN before contact is calculated to be 0.5 eV. This value is evidently smaller than the VBO of 0.7 eV for S2 (VBO₂) and 0.9 eV for S3 (VBO₃). The latter two values are larger due to the upward band bending at the GaN surface as explained above.

In summary, our study on the interface region between GaN and Al₂O₃ using XPS yields two main findings: (1) The growth of a thin interfacial GaO_x layer following the ALD of Al₂O₃ is still observed, despite the use of TMA-only cycles in the initial stage to convert the native oxide to Al₂O₃. This suggests a lower limit to the native oxide thickness so that the resultant Al₂O₃ layer is thick enough to block GaN oxidation during subsequent Al₂O₃ deposition involving the oxidizing agent. (2) The BE of the Ga 3d and N 1s spectra

are decreased and the extracted VBO between GaN/Al₂O₃ is increased when the thickness of the Al₂O₃ is increased, whereas the Al 2p spectra are unaffected. These observations could be consistently explained by the upward surface band bending due to a polarization induced negative surface bound charge in the Ga-face GaN and they highlight an intrinsic limitation of the XPS method for band offset determination.

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