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Impact of post-deposition annealing on interfacial chemical bonding states between AlGa_{0.5}N and ZrO₂ grown by atomic layer deposition

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The effect of post-deposition annealing on chemical bonding states at interface between Al_{0.5}Ga_{0.5}N and ZrO₂ grown by atomic layer deposition (ALD) is studied by angle-resolved x-ray photoelectron spectroscopy and high-resolution transmission electron microscopy. It has been found that both of Al-O/Al 2p and Ga-O/Ga 3d area ratio decrease at annealing temperatures lower than 500 °C, which could be attributed to “clean up” effect of ALD-ZrO₂ on AlGa_{0.5}N. Compared to Ga spectra, a much larger decrease in Al-O/Al 2p ratio at a smaller take-off angle θ is observed, which indicates higher effectiveness of the passivation of Al-O bond than Ga-O bond through “clean up” effect near the interface. However, degradation of ZrO₂/AlGa_{0.5}N interface quality due to re-oxidation at higher annealing temperature (>500 °C) is also found. The XPS spectra clearly reveal that Al atoms at ZrO₂/AlGa_{0.5}N interface are easier to get oxidized as compared with Ga atoms. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4914351>]

AlGa_{0.5}N/GaN high electron mobility transistors (HEMTs) have been used extensively for high frequency,¹ high power,² and low noise applications.³ However, surface-related defect states associated to the sub-oxide layer formed at AlGa_{0.5}N barrier layer or possible GaN cap layer surface can result in large current leakage⁴ and severe current collapse at high frequency.⁵ Metal-insulator-semiconductor HEMTs (MISHEMTs) utilizing a dielectric layer as the gate insulator and surface passivation layer are one proposed method to mitigate the above issues.^{6,7} Due to its high dielectric constant along with large conductance band offset (CBO) and valance band offset (VBO) with respect to GaN substrate,⁸ ZrO₂ is a promising dielectric material candidate for AlGa_{0.5}N/GaN MISHEMTs. Excellent electrical characteristics of GaN-based MISHEMTs utilizing ZrO₂ as gate dielectrics are reported recently.^{9–14} In addition, from device fabrication point of view, post-deposition annealing (PDA) could serve as an effective way to improve the interfacial properties between high-k dielectric layer and GaN-based substrates. However, even though AlGa_{0.5}N has been extensively utilized in GaN HEMTs, few studies have been carried out on the interfacial structure and chemical bonding states at the interface between ZrO₂ and AlGa_{0.5}N subjected to post-deposition annealing. In this paper, a detailed investigation of the impact of post deposition annealing on interfacial chemical bonding states between atomic layer deposited (ALD) ZrO₂ and Al_{0.5}Ga_{0.5}N is carried out by using angle-resolved X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HR-TEM).

ZrO₂ dielectric layers were deposited on Al_{0.5}Ga_{0.5}N-on-sapphire substrates by using ALD. The un-doped

Al_{0.5}Ga_{0.5}N-on-sapphire wafers were grown by Metal Organic Chemical Vapor Deposition (MOCVD) using a commercial reactor. An Al to Ga ratio of 1:1 in the AlGa_{0.5}N layer was intentionally used to facilitate the comparison of the roles of Al and Ga at the interface upon annealing. The Al_{0.5}Ga_{0.5}N-on-sapphire wafers were initially degreased in acetone and subsequently rinsed by isopropyl alcohol (IPA) both for 10 min. Before loaded into the ALD chamber, samples were treated by buffered oxide etchant (BOE) solution to remove surface native oxide and followed by a rinse in de-ionized (DI) water. For ALD, the tetrakis-(dimethylamido)-zirconium and H₂O were used as the precursors. Chamber pressure and substrate temperature were set at 0.6 Torr and 250 °C, respectively. During the deposition, sequential 400 ms and 40 ms pulse of H₂O and Zr sources were introduced into the chamber separately. After each pulse, the chamber was purged with N₂ for 6 s to remove excess precursors and by-product gases. The growth rate for ZrO₂ was around 0.09 nm per ALD cycle. After deposition, different post-deposition anneals using rapid thermal annealing (RTA) in N₂ atmospheres for 30 s were performed in the temperature range from 300 to 700 °C. Samples with 2 nm thick ZrO₂ on Al_{0.5}Ga_{0.5}N surface were utilized for XPS measurements. The XPS measurements were carried out using a monochromatic Al K α X-ray source of energy 1486.7 eV. The spectra are curve-fitted with a combination of Gaussian and Lorentzian line shapes using a Shirley-type background subtraction. All peaks were referenced to the C 1s peak at 284.6 eV to compensate for any variations in the peak core-level positions due to binding energy (BE) shift caused by surface charging. The take-off angle θ defined as the elevation angle with respect to the sample surface was changed to vary the photoelectron escape depth λ according to

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$$\lambda = \lambda_0 \sin \theta, \quad (1)$$

where λ_0 is the inelastic mean free path of photoelectrons. By decreasing of θ to shorten the probing depth, more sensitive analysis of chemical bonding states near the interface between ZrO_2 layer and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ substrate can be obtained.

The Al 2*p* and Ga 3*d* core-level spectra obtained at two take-off angles θ of 90° and 15° for 2 nm thick ZrO_2 on AlGa_{0.5}N samples under different PDA temperatures are shown in Figs. 1 and 2, respectively. Al 2*p* spectrum in Figs. 1(a) and 2(a) could be deconvoluted into two components, corresponding to the Al-N and Al-O bonds, while Ga-N and Ga-O bond components are observed for Ga 3*d* spectrum as shown in Figs. 1(b) and 2(b). The existence of the Al-O and Ga-O spectrum for the as-deposited sample (indicated by N.A in Figs. 1 and 2) could be attributed to the parasitic oxidation of the AlGa_{0.5}N surface after cleaning during ALD deposition process.^{15,16} As can be seen, the interfacial chemical bonding states for ALD- ZrO_2 on AlGa_{0.5}N are highly depend on the annealing temperatures. Fig. 3 plots the dependence of Al-O to Al 2*p* and Ga-O to Ga 3*d* XPS peak area ratio as a function of the annealing temperatures at take-off angles of 15° and 90°. For both take-off angles, the Al-O/Al 2*p* and Ga-O/Ga 3*d* area ratios decrease with the increase in annealing temperature when the RTA temperature is lower than 500 °C. This could be ascribed to the passivation of sub-oxide interfacial states through the “clean up” effect that is widely reported for ALD deposited high-*k* dielectrics on III-V semiconductor substrates.^{17–20} However, with the further increment in annealing temperatures, re-growth of the sub-oxide interfacial layer is evidenced by the increase in Al-O/Al 2*p* and Ga-O/Ga 3*d* area ratios for both take-off angles. In fact, the annihilation or formation of the interfacial layer can be further confirmed by

FIG. 1. The measured (open circles) and fitted (lines) XPS Al 2*p* (a) core-level spectra and Ga 3*d* (b) core-level spectra for 2 nm ALD- ZrO_2 on $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ samples at take-off angle θ of 90° under different PDA temperatures. The as-deposited sample is indicated as N.A.

FIG. 2. The measured (open circles) and fitted (lines) XPS Al 2*p* (a) core-level spectra and Ga 3*d* (b) core-level spectra for 2 nm ALD- ZrO_2 on $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ samples at take-off angle θ of 15° under different PDA temperatures. The as-deposited sample is indicated as N.A.

HR-TEM. Cross-sectional TEM micrographs for as-deposited sample (N.A) and samples annealed at 500 °C and 700 °C are shown in Fig. 4. An interfacial layer is observed for the as-deposited sample (Fig. 4(a)). While, an abrupt interface without any interfacial layer for the sample annealed under 500 °C is presented by HR-TEM. With the further increase in annealing temperatures to 700 °C, re-formation of the interfacial layer is observed as shown in Fig. 4(c). Similar phenomenon was observed for ALD- ZrO_2 on GaN in our earlier publication (Ref. 21), which may share the same mechanisms of annihilation/formation of the interfacial layer discussed in this letter. On the other hand, it can be seen from Figs. 1 and 2 that shifts

FIG. 3. Change of integrated XPS intensity ratios of Al-O bond to Al 2*p* and Ga-O bond to Ga 3*d* for $\text{ZrO}_2/\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ samples measured at take-off angles θ of 15° and 90° under different PDA temperatures. The as deposited sample is indicated as N.A, and the dashed lines are a guide for the eye to illustrate the trend.

FIG. 4. Cross-sectional TEM images of the ZrO_2 dielectric layers on $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$: (a) as-deposited (N. A), (b) annealed at 500°C in N_2 for 30 s, and (c) annealed at 700°C in N_2 for 30 s. The interfacial layer is indicated as IL.

of binding energy of Al-N and Ga-N bonds are highly related to Al-O/Al $2p$ and Ga-O/Ga $3d$ ratios. This could be due to surface Fermi-level pinning caused by interfacial oxide related defects, which is consistent with our earlier observations.²¹

As a ternary III-nitride semiconductor, interfacial chemical bonding states between ZrO_2 and AlGa N could be more complicated compared to ZrO_2/GaN . This is evidenced by the decrease or increase rate of area ratio upon annealing temperatures in Fig. 3. The influence of annealing temperatures on both of the Al-O/Al $2p$ and Ga-O/Ga $3d$ area ratios at a smaller θ are more pronounced, which suggests that the annihilation/formation of the interfacial layer is mainly occurred within a narrow depth near the AlGa N surface. More importantly, compared to Ga spectra, the Al-O/Al $2p$ area ratio shows more obvious variations with respect to the PDA temperatures at θ of 15° . This implies that, at annealing temperatures lower than 500°C , the passivation of Al-O bonds at $\text{ZrO}_2/\text{AlGaN}$ interface could be more effective compared with Ga-O bonds through the “clean up” effect. On the other hand, when the annealing temperature is further increased, Al atoms at the $\text{ZrO}_2/\text{AlGaN}$ interface are more likely to get oxidized than Ga atoms due to the higher reactivity of Al atoms.^{22–25}

In conclusion, the effect of post-deposition annealing on interfacial chemical bonding states for ALD- ZrO_2 on $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ is studied by angle-resolved XPS and HR-TEM. The experimental results reveal that the $\text{ZrO}_2/\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ interface quality can be improved by the annihilation of the sub-oxide layers through post-deposition annealing in N_2 ambient at a temperature below 500°C , suggesting the presence of the “clean up” effect of ALD- ZrO_2 on AlGa N . When compared with Ga spectra, a much larger decrease in Al-O/Al $2p$ ratio at a smaller take-off angle θ is observed, which suggests higher effectiveness of the passivation of Al-O bond than Ga-O bond through the “clean up” effect near the interface. On the other hand, re-formation of interfacial layer at higher annealing temperatures is also found and Al atoms

are more likely to be oxidized compared to Ga atoms. The above results provide important process guidelines for the use of ALD ZrO_2 as the high-k gate dielectrics and passivation layers for AlGa N /Ga N HEMTs.

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