Band alignment modulation of ALD-prepared Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunction interface by deposition temperature

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The band alignment between oxygen plasma-assisted atomic layer deposition (ALD) Al$_2$O$_3$ films and β-Ga$_2$O$_3$ (-201) substrates under different deposition temperatures was characterized by X-ray photoelectron spectroscopy (XPS). As the deposition temperature increased from 30 to 200 °C, all the heterojunctions exhibited a type-I alignment. The bandgap of Al$_2$O$_3$ enlarged from 6.26 ± 0.1 to 6.81 ± 0.1 eV, leading to the conduction band offset (CBO) varying linearly from 1.39 ± 0.1 to 1.95 ± 0.1 eV, while the valence band offset (VBO) was insensitive. This difference was attributed to Al ion deficiency and hydroxyl groups induced by the inadequate reaction of trimethylaluminium (TMA) under low deposition temperatures, which was proved by secondary ion mass spectrometry (SIMS) and Fourier-transform infrared spectroscopy (FTIR). These findings could facilitate the design of the CBO-controllable Al$_2$O$_3$/β-
Ga$_2$O$_3$ heterojunction through deposition temperature.

I. INTRODUCTION

$\beta$-Ga$_2$O$_3$ is one of the emerging wide-gap semiconductors for next-generation high-power electronic applications, which has gained extensive attention in recent years.$^{1-3}$ The theoretical maximal breakdown field of $\beta$-Ga$_2$O$_3$ is expected to be $\sim$ 8MV/cm due to its ultrawide bandgap (4.6-4.9 eV),$^4$ and the Baliga's figure of merit ($\varepsilon \mu E_{br}^3$) is as high as 3444,$^{5}$ which exceeds the value of GaN and SiC.$^6$ Besides these excellent material properties, its mass production of high-quality single crystal $\beta$-Ga$_2$O$_3$ can be acquired by low-cost melt growth methods such as edge-defined film-fed (EDFG) and floating-zone (FZ) for commercial utilization.$^{7,8}$

Over the past years, high-power metal-insulator semiconductor field-effect transistors (MISFETs) based on $\beta$-Ga$_2$O$_3$ have been demonstrated.$^{9,10}$ For practical MISFETs, the choice of gate insulator layer-plays an important role in obtaining high-performance transistors, the leakage current and on/off current ratio are mainly determined by the semiconductor/gate insulator interface. Up to now, several insulators including SiO$_2$,$^{11}$ Al$_2$O$_3$,$^{12}$ AlN,$^{13,14}$ etc. have been successively investigated for applications of $\beta$-Ga$_2$O$_3$ based FETs. Among which, Al$_2$O$_3$ is implemented extensively because of its moderately large bandgap (6.4-6.9 eV) and high dielectric constant of ~9. To evaluate the anti-leakage current stability of the gate insulator, the band alignment analysis of the gate insulator/$\beta$-Ga$_2$O$_3$ is necessary to calculate the VBO and CBO.
across the gate insulator/bulk material.

Kamimura *et al.* investigated the band offset of ALD prepared Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunction using X-ray photoelectron spectroscopy (XPS), and a bandgap for Al$_2$O$_3$ of 6.8 ± 0.2 eV was observed. Meanwhile, the VBO and CBO were calculated to be 0.7 ± 0.2 and 1.5 ± 0.2 eV, respectively. Carey *et al.* compared the influence of different deposition methods on the band alignment of Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunctions between radio-frequency (RF) magnetron sputtering and ALD methods. The bandgaps of Al$_2$O$_3$ fabricated by the two methods were both 6.9 eV, while the CBO of 3.16 eV (2.23 eV) and the VBO of -0.86 eV (-0.07 eV) were measured for sputtering (ALD) method, respectively. Hung *et al.* quantitatively investigated the CBO and effects of interface fixed charges on ALD prepared Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunctions, where a CBO of 1.7 eV was obtained. Thus, it can be concluded that the VBO and CBO of Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunctions are influenced by the preparation method and processing parameter, as well as the deposition temperature. However, a systematic investigation concerning the band alignment-temperature dependence of Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunction is absent so far. Furthermore, a tunable band alignment is desired for the degree of design freedom to meet specific demands. For instance, alloying processes such as (Al$_x$Ga$_{1-x}$)$_2$O$_3$ and Hf$_x$Al$_{1-x}$O were adopted to characterize the VBO and CBO modulations of β-Ga$_2$O$_3$-based heterojunctions. However, this method is limited by its complex procedure, and the prepared alloys are often subjected to the bowing behavior.

Herein, this work presents the temperature-dependent band alignment of Al$_2$O$_3$/β-
Ga$_2$O$_3$ heterojunction, in which the Al$_2$O$_3$ films were prepared by an oxygen plasma-assisted ALD method. The band alignment and band offset values were characterized and determined. At last, the difference in the temperature dependence of VBO and CBO was further discussed and proved by SIMS and FTIR.

II. EXPERIMENTAL

All Al$_2$O$_3$ films in this study were deposited using ALD with trimethylaluminum (TMA, purity: 99.999%, Fornano, Suzhou, China) and O$_2$ plasma as Al and O precursors, respectively. Prior to the Al$_2$O$_3$ deposition, $\beta$-Ga$_2$O$_3$ substrates were cleaned in solvent (acetone/isopropanol/deionized water) to remove the residual contaminations, and then were loaded into ALD reactor (Picosun R-200 Advanced, Finland) for Al$_2$O$_3$ deposition. One growth cycle consisted of 0.1 s TMA pulse, 10 s N$_2$ purge, 8 s O$_2$ plasma pulse, and 10 s N$_2$ purge. The TMA was maintained at 18 $^\circ$C for a stable vapor pressure and dose, and the O$_2$ gas flow rate was fixed at 150 sccm using a remote plasma generator (Advanced energy, USA) with the power of 2500 W. The reaction chamber pressure was kept at ~1000 Pa. Three types of samples were prepared for XPS measurements: (1) bulk (-201) $\beta$-Ga$_2$O$_3$ substrates (Sn-doping, $4.2 \times 10^{18}$ cm$^{-3}$) grown by floating-zone method, (2) 40 nm-thick Al$_2$O$_3$ films deposited on $\beta$-Ga$_2$O$_3$ substrates under 30, 50, 100, 150 and 200 $^\circ$C, respectively, and (3) 3nm-thick Al$_2$O$_3$ films deposited on $\beta$-Ga$_2$O$_3$ substrates under 30, 50, 100, 150 and 200 $^\circ$C, respectively. The XPS measurements were carried out by using a monochromatic Al Kα1 X-radiation source (1486.7 eV). All high-resolution binding energy spectra were collected in a step
of 0.05 eV. The C 1s peak located at 284.8 eV was adopted as the calibration reference. Reflection electron energy loss spectroscopy (REELS) was used to determine the bandgap \( E_g \) of the deposited films. Secondary ion mass spectrometry (SIMS) (PHI Adept 1010, Japan) with Cs primary ion beam with an energy of 3 keV was employed for profiling Ga, Al, and H elements concentration distributions. The Fourier-transform infrared spectroscopy (FTIR) ranged from 4000-1000 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\) was performed using a TENSOR II Bruker spectrometer at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the O 1s core-level REELS spectra of 40 nm-thick \( \text{Al}_2\text{O}_3 \) films deposited under different temperatures, the bandgap \( E_g \) of the deposited \( \text{Al}_2\text{O}_3 \) film was defined as the intercept energy between flat and linear slope regions. As the deposition temperature increases, the linear slope region shifts to a higher loss energy, leading to the enlargement of the bandgap. For the sample deposited under 30 °C, the extracted \( E_g \) is 6.26 ± 0.1 eV, and the \( E_g \) rises to 6.81 ± 0.1 eV as the deposition temperature increased to 200 °C. Detailed \( E_g \) under different deposition temperatures were listed in Table 1.
Fig. 1. O 1s core-level REELS spectra of 40 nm-thick Al₂O₃ films deposited on β-Ga₂O₃ substrate under different deposition temperatures.

To investigate the band alignment of the Al₂O₃/β-Ga₂O₃ heterojunction, high-resolution XPS was utilized to record the core-level spectra, and the VBM position of Al₂O₃ and β-Ga₂O₃ were estimated through a linear extrapolation of the leading edge to the baseline of the valence band spectra. According to Kraut's theory, the VBO (ΔEᵥ) can be calculated by the following formula:\(^\text{19}\)

\[
\Delta E_v = \left( E_{\text{Ga3d}}^{\text{Ga}_2\text{O}_3} - E_{\text{VBM}}^{\text{Ga}_2\text{O}_3} \right) - \left( E_{\text{Al2p}}^{\text{Al}_2\text{O}_3} - E_{\text{VBM}}^{\text{Al}_2\text{O}_3} \right) + \left( E_{\text{Heterojunction}}^{\text{Ga3d}} - E_{\text{Heterojunction}}^{\text{Al2p}} \right)
\]

where \(E_{\text{Ga3d}}^{\text{Ga}_2\text{O}_3}\) and \(E_{\text{VBM}}^{\text{Ga}_2\text{O}_3}\) correspond to the peak positions of the Ga 3d core level and VBM for bulk β-Ga₂O₃, respectively. \(E_{\text{Al2p}}^{\text{Al}_2\text{O}_3}\) and \(E_{\text{VBM}}^{\text{Al}_2\text{O}_3}\) are the peak positions of the Al 2p core level and VBM for 40 nm-thick Al₂O₃ film, respectively. \(E_{\text{Heterojunction}}^{\text{Ga3d}}\) and \(E_{\text{Heterojunction}}^{\text{Al2p}}\) represent the peak positions of the Ga 3d and Al 2p core levels in the heterojunction, respectively.

Figure 2(a) and 2(b) present the binding energy differences for 40 nm-thick Al₂O₃ film (Al 2p) and bulk β-Ga₂O₃ (Ga 3d), respectively. The VBM positions for Al₂O₃ and β-Ga₂O₃ are 3.47 and 3.53 eV, respectively. The core levels for Al 2p and Ga 3d are located at 74.48 (Al-O bond) and 20.37 eV (Ga-O bond), respectively, consistent with previous reports\(^\text{13,15,16}\). From Eq. (2), the VBO of the Al₂O₃/β-Ga₂O₃ heterojunction deposited under 30 °C was calculated to be 0.22 ± 0.05 eV. Based on the obtained VBO, the CBO (\(\Delta E_c\)) was subsequently calculated by
\[ \Delta E_C = E_{g}^{Al_2O_3} - E_{g}^{Ga_2O_3} - \Delta E_V \]  

where \( E_{g}^{Al_2O_3} \) and \( E_{g}^{Ga_2O_3} \) are the bandgap of \( Al_2O_3 \) and \( \beta-Ga_2O_3 \), respectively. According to our previous report, the estimated \( E_{g}^{Ga_2O_3} \) was \( 4.65 \pm 0.1 \) eV,\(^\text{20}\) which was extracted from O 1s core-level REELS spectrum. Based on the aforementioned, the CBO was calculated to be \( 1.39 \pm 0.1 \) eV. Similarly, the VBOs and CBOs for \( Al_2O_3/\beta-Ga_2O_3 \) heterojunctions deposited under higher temperatures were evaluated, as shown in Table 1.
Fig. 2. Binding energy differences of (a) Al 2p and VBM for bulk Al₂O₃, (b) Ga 3d and VBM for bulk β-Ga₂O₃, and (c) Al 2p and Ga 3d for the Al₂O₃/β-Ga₂O₃ heterojunction deposited at 30 °C.

Table I. The bandgaps of Al₂O₃ films, the VBOs and CBOs for Al₂O₃/β-Ga₂O₃ heterojunctions, and the O/Al atoms ratio in Al₂O₃ films deposited under different temperatures. The standard deviations for bandgap, VBO, and EBO ration are ± 0.1, ± 0.05, and ± 0.1 eV, respectively.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Al₂O₃ bandgap (eV)</th>
<th>VBO (eV)</th>
<th>EBO (eV)</th>
<th>O/Al atoms ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6.26</td>
<td>0.22</td>
<td>1.39</td>
<td>1.97</td>
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<tr>
<td>50</td>
<td>6.35</td>
<td>0.21</td>
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<td>0.21</td>
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<td>150</td>
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<td>0.20</td>
<td>1.86</td>
<td>1.61</td>
</tr>
<tr>
<td>200</td>
<td>6.81</td>
<td>0.21</td>
<td>1.95</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The detailed energy band alignment of Al₂O₃/β-Ga₂O₃ heterojunctions deposited under different temperatures was plotted, as shown in Figure 3. All the band alignments exhibit a typical straddled (type-I) feature. With deposition temperature rising from 30 to 200 °C, the bandgap of Al₂O₃ increases from 6.26 ± 0.1 to 6.81 ± 0.1 eV, and the CBO of Al₂O₃/β-Ga₂O₃ heterojunction increases from 1.39 ± 0.1 to 1.95 ± 0.1 eV by 0.56 eV. While the VBO is insensitive to the Al₂O₃ film deposition temperature and keeps around 0.21 ± 0.05 eV.
FIG. 3. The band alignment of Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunctions under different deposition temperatures.

The CBOs and VBOs of Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunction as a function of deposition temperature was plotted in Figure 4(a). The CBO exhibits a ~50 times higher linear deposition-temperature dependence (the slope coefficient is 0.00333) than VBO (the slope coefficient is -0.000006). This implies that the CBO for the Al$_2$O$_3$/β-Ga$_2$O$_3$ system can be linearly modulated by the ALD temperature, which is more controllable and easier than alloying method such as (Al$_x$Ga$_{1-x}$)$_2$O$_3$ and Hf$_x$Al$_{1-x}$O.$^{17,18}$

To figure out this CBO linear deposition-temperature dependence, the Al/O atoms ratio and bandgap value for 40 nm-thick Al$_2$O$_3$ film as a function of deposition temperature were also presented, as shown in Figure 4(b). The O/Al atoms ratio decreases linearly with the deposition temperature, the O/Al atoms ratio for 40 nm-thick Al$_2$O$_3$ film prepared under 30 and 200 °C are 1.97 and 1.40, respectively. While the bandgap of Al$_2$O$_3$ film enlarges linearly with the deposition temperature. These results indicate that the VBM position is insensitive to the deposition temperature, while
the increased deposition temperature leads to the O/Al atoms ratio decreases to meet the ideal stoichiometry of Al₂O₃ (3:2). The enlarged bandgap further shifts the CBM of Al₂O₃ to a higher energy, resulting in an increased CBO which is sensitive to the deposition temperature.

![Graphs showing temperature dependence of CBO and VBO, bandgap, and O/Al ratio](image)

**Fig. 4.** Temperature dependence of (a) CBO and VBO, (b) bandgap and O/Al ratio of Al₂O₃ in the range of 30 - 200 °C.

Next, SIMS was utilized to examine the H concentration distribution in the Al₂O₃ films, the result is shown in Figure 5. The H concentration in the Al₂O₃ film grown under 200 °C is ~2.92 × 10²¹ atoms/cc, which is obviously lower than the value for the sample deposited at 30 °C (~6.88 × 10²¹ atoms/cc). The inset of Figure 5 displays the Al, Ga, and H elements distributions in Al₂O₃/β-Ga₂O₃ heterojunction, the abrupt
variations of the Al and Ga elements indicate the high-quality interface between Al₂O₃ and β-Ga₂O₃ substrate. To further track the excessive O and H elements in Al₂O₃ films, FTIR spectra were adopted to analyze the components. Figure 6 shows the FTIR spectra of Al₂O₃ films grown by ALD under temperatures of 30 and 200 °C. Obviously, a few peaks around 1600 cm⁻¹ which are assigned to C-H, C=O, and C=C stretching vibration emerge in the Al₂O₃ deposited under 30 °C,²¹,²² while the peak at 3750 cm⁻¹ is related to hydroxyl group (-OH).²³ In contrast, the Al₂O₃ film deposited at 200 °C exhibits weak peaks around both 3750 cm⁻¹ and 1600 cm⁻¹. These results imply that there are more C-H, C=O, and C=C bonds, accompanied with hydroxyl groups in the Al₂O₃ film under low deposition temperature. It can be attributed to the inadequate reaction between TMA and O₂ plasma. These FTIR spectra features are also in good agreement with SIMS results.

![FTIR spectra](image)

**Fig. 5.** H concentration in Al₂O₃ films grown under deposition temperatures of 30 °C and 200 °C derived from SIMS measurements. The inset plots H, Al, Ga concentrations with different depths at 30 °C.
Fig. 6. FTIR spectra of Al$_2$O$_3$ films grown by ALD under deposition temperatures of 30 and 200 °C.

Previous studies revealed that under low-deposition temperature (below the crystallization temperature), the Al$_2$O$_3$ film density increases with the deposition temperature. For Al$_2$O$_3$ film deposited under 30 °C, the lower film density and high O/Al atoms ratio (exceeds 3:2) indicate the film is loosened with high-density vacancies and cavities. In our deposition process, the O$_2$ plasma with high energy makes the film fully oxidized, while the low deposition temperature leads to the inadequate reaction of TMA. The dissociative Al ions and hydroxy groups induced by the un-reacted TMA can fill the vacancies and cavities in the films, which were deposited under low temperatures. First-principles calculations results indicated both the VBM of Al$_2$O$_3$ and Ga$_2$O$_3$ are derived from O 2p orbitals, while the VBM for Al$_2$O$_3$ and Ga$_2$O$_3$ mainly consist of Al 3s and Ga 4s orbitals, respectively. The deficiency of Al ions as well as hydroxy groups and vacancies dominate the CBM position, making the CBO sensitive to the deposition temperature. As the deposition temperature increases to 200 °C, the dense Al$_2$O$_3$ film with ideal elemental chemical ratio restrains the vacancies
and cavities appearance, then the Al$_2$O$_3$ bandgap is enlarged. While the adequate O ions from O$_2$ plasma ensure the VBM of Al$_2$O$_3$ pinned at a specific energy, thus the VBO is immune to the deposition temperature.

**IV. SUMMARY AND CONCLUSIONS**

In summary, we have investigated the band alignment modulation of ALD-prepared Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunction. As the deposition temperature increased from 30 to 200 °C, all the heterojunctions exhibited type-I alignment characteristic. The bandgap of Al$_2$O$_3$ enlarged from 6.26 ± 0.1 to 6.81 ± 0.1 eV, leading the conduction band offset (CBO) varying linearly from 1.39 ± 0.1 to 1.95 ± 0.1 eV, while the valence band offset (VBO) was insensitive. This difference was attributed to the Al ions deficiency and hydroxyl groups induced by the inadequate reaction of TMA under low deposition temperatures. These finding could facilitate the design of the CBO-controllable Al$_2$O$_3$/β-Ga$_2$O$_3$ heterojunction through deposition temperature.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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