Band Alignment of Atomic Layer Deposited SiO2 and Al2O3 on (AlxGa1-x)2O3 for x = 0.2-0.65

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(AIₓGa₁₋ₓ)₂O₃ is attracting attention for use in heterostructure devices grown on Ga₂O₃ substrates. The band alignments of amorphous, atomic layer deposited Al₂O₃ and SiO₂ on (AIₓGa₁₋ₓ)₂O₃ for x = 0.2-0.65 have been determined using high resolution X-ray photoelectron spectroscopy. The (AIₓGa₁₋ₓ)₂O₃ was grown by continuous composition spread Pulsed Laser Deposition (CCS-PLD). The band alignments are type I (nested gap) in all cases, with conduction band offsets ranging from 1.57-0.67 eV for Al₂O₃ on (Alₓ₂Ga₀₋ₓ)₂O₃ to (AIₓGa₁₋ₓ)₂O₃ and 2.35-1.40 eV for SiO₂ on these same compositions. Correspondingly, the valence band offsets are all >1.25 eV for SiO₂ and 0.23-0.33 eV for Al₂O₃ over this composition range. While these are the first reports for Al₂O₃ on (AIₓGa₁₋ₓ)₂O₃ over such a wide composition range, our results differ by up to 0.4 eV in conduction band offsets from past studies of SiO₂ on (AIₓGa₁₋ₓ)₂O₃ of a more limited composition range, which themselves have shown variations of up to 0.5 eV for conduction band offsets on nominally the same composition. These differences emphasize the influence of experimental conditions in determining band alignments.

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The lateral variation of the Al content of a \((\text{Al}_{x}\text{Ga}_{1-x})_2\text{O}_3\) thin film grown by CCS-PLD using a target consisting of semicircular \(\text{Al}_2\text{O}_3\) and \(\text{Ga}_2\text{O}_3\) segments is shown in Figure 2a. Energy-dispersive X-ray spectroscopy (EDX) was used for the spatially resolved chemical analysis, where a Nova Nanolab 200 system by FEI company was employed. The sample was deposited at a growth temperature of 650°C and an oxygen pressure 0.08 mbar on a two inch in diameter (100) MgO substrate. The Al concentration varies between 0.15 and 0.70, as shown in Figure 2b and has a slight S-shaped dependence along the gradient direction, in agreement with calculations.\(^{13}\) Along lines perpendicular to the gradient direction the Al concentration is in principle constant. Figure 3 shows a false color representation of X-ray diffractograms along the compositional gradient. As discussed above, there is pure monoclinic phase up to \(\sim 40-45\) at.\%, then a mixed phase with \(\gamma-(\text{Al}_{x}\text{Ga}_{1-x})_2\text{O}_3\) is present. Above \(\sim 50-55\) at.\%, the films show pure \(\gamma\)-phase. More details of the growth are given elsewhere.\(^{6,13}\)

The ALD layers were deposited at 200°C in remote plasma mode in a Cambridge Nano Fiji 200 using a trimethylaluminum precursor or Tris (dimethylamino) silane and an inductively coupled plasma (ICP) at 300 W to generate atomic oxygen.\(^{26–29}\) For substrate cleaning prior to deposition, a rinse sequence consisting of acetone and IPA was followed by drying in filtered \(\text{N}_2\), and finally ozone exposure for 15 min. After this substrate cleaning, samples were directly loaded into the deposition systems within a cleanroom environment to avoid contamination of the deposited films. Both thick (200 nm) and thin...
Figure 5. XPS spectra of core levels to valence band maximum (VBM) for (a) reference (Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> with 20% and 35% Aluminum, (b) reference (Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> with 50% and 65% Aluminum, and (c) ALD thick film Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. The intensity is in arbitrary units (a.u.).

Figure 6. Bandgap of (a) (Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> determined using the onset of the plasmon loss feature in O 1s photoemission spectrum, (b) ALD SiO<sub>2</sub>, and (c) ALD Al<sub>2</sub>O<sub>3</sub> where both deposited films’ bandgap was determined by Reflection Electron Energy Loss Spectra. The intensities are in arbitrary units (a.u.).
(1.5 nm) layers of the dielectrics were deposited for measuring both bandgaps and core levels on the $\beta-(Al,Ga)_{2}O_{3}$.\(^{30}\)

We used XPS survey scans to establish the chemical state of the SiO$_2$, Al$_2$O$_3$, and the $(Al,Ga)_{2}O_{3}$ samples. The XPS system was a Physical Instruments ULVAC PHI, with an Al X-ray source (energy 1486.6 eV, source power 300W), analysis size of 100 μm diameter, a take-off angle of 50° and acceptance angle of ± 7 degrees. The electron pass energy was 23.5 eV for high-resolution scans and 93.5 eV for survey scans. The total energy resolution of this XPS system is about 0.03 eV.\(^{27-30}\)

To avoid sample charging, charge compensation employed an electron flood gun and a simultaneous ion beam. C\(_1s\) core levels of the surface adsorbate (284.8 eV) were used to calibrate the binding energy. Only the relative energy position is needed to determine the valence band offsets, so the absolute energy calibration for a sample has no effect on that number.\(^{22,23}\) The samples were electrically insulated from the chuck to avoid uneven charge dispersion along the sample. All electron analyzers and equipment were grounded. Differential charging was not observed in any of the samples with the use of the electron gun. The SiO$_2$ and Al$_2$O$_3$ bandgaps were obtained from Reflection Electron Energy Loss Spectroscopy (REELS)\(^{32,33}\) using a 1 kV electron beam and hemispherical electron analyzer. The bandgaps of the $(Al,Ga)_{2}O_{3}$ for each composition were obtained from XPS energy loss measurements of the O1S peak. This is conveniently done at the same time as the band alignment measurements.

### Results and Discussion

The XPS survey scans from the different compositions of $(Al,Ga)_{2}O_{3}$ are shown in Figure 4a. The samples show only the lattice constituents. Figure 4b shows the survey spectra for the thick (200 nm) dielectrics of ALD SiO$_2$ and Al$_2$O$_3$, thin (1.5 nm) SiO$_2$ and Al$_2$O$_3$ on $\beta-(Al,Ga)_{2}O_{3}$, labelled here as AGO, and the $(Al,Ga)_{2}O_{3}$ sample for reference.

Figure 5 shows high resolution XPS spectra for the vacuum-core delta regions of four different $(Al,Ga)_{2}O_{3}$ compositions, namely $x = 0.2$, 0.35, 0.5 and 0.65 in (a), $x = 0.2$ and 0.35 in (b), along with the SiO$_2$ and Al$_2$O$_3$ in (c). The VBM were 3.6 ± 0.2 eV for $\beta-(Al_{0.2}Ga_{0.8})_{2}O_{3}$, 3.3 eV for $(Al_{0.35}Ga_{0.65})_{2}O_{3}$, 2.9 eV for $(Al_{0.5}Ga_{0.5})_{2}O_{3}$ and 2.6 eV for $(Al_{0.65}Ga_{0.35})_{2}O_{3}$. The valence band offsets are then obtained by measuring the shift of the core levels for the heterostructure samples with the thin dielectric on top of the different compositions of $(Al,Ga)_{2}O_{3}$.\(^{35}\) We also measured the bandgaps of the $(Al,Ga)_{2}O_{3}$ at the compositions of interest, as shown in Figure 6a, from the separation between the core level peak energy and the onset of inelastic (plasmon) losses in each O 1s photoemission spectra.\(^{35}\) The respective bandgaps were 5.1 eV for $(Al_{0.2}Ga_{0.8})_{2}O_{3}$, 5.35 eV for $(Al_{0.35}Ga_{0.65})_{2}O_{3}$, 5.65 eV for $(Al_{0.5}Ga_{0.5})_{2}O_{3}$ and 5.90 eV for $(Al_{0.65}Ga_{0.35})_{2}O_{3}$. These are in excellent agreement with the relationship reported previously for the compositional dependence of bandgap ($E_g$) of $(Al,Ga)_{2}O_{3}$, namely\(^{1,7,36}\):

\[
E_g = (4.75 + 1.87x) \text{eV}
\]

Using this relationship, we would expect values of 5.1 eV for $x = 0.2$, 5.4 eV for $x = 0.35$, 5.68 eV for $x = 0.50$ and 5.97 eV for $x = 0.65$, i.e. the differences from our experimental values are <0.07 eV across the composition range studied here. Values of the indirect bandgap using the formula $E_g = 4.637 + 1.87x$, determined by Schmidt-Grund et al.\(^{3}\) on a similar CCS-PLD sample by using spectroscopic ellipsometry, are 5.01 eV, 5.29 eV, 5.57 eV and 5.85 eV for $x = 0.2, 0.35, 0.5$ and 0.65, respectively, which is in good agreement to the values determined by XPS. Other experimental values for similar compositions reported from studies by Feng et al.\(^{25,26}\) include 5.1 eV ($x = 0.35$), 5.3 eV ($x = 0.33$), 5.43 eV ($x = 0.30$), 5.2 eV ($x = 0.40$), 5.64 eV ($x = 0.49$), and 5.4 eV ($x = 0.53$). Obviously, within similar groups of samples in those cases, there was variation of ∼0.2 eV. Wakabayashi et al.\(^{20}\) reported that strain in layers of $(Al,Ga)_{2}O_{3}$ might lead to bowing of the bandgap with composition. Figures 6b and 6c shows the REELS spectra to determine the bandgap of the SiO$_2$ and Al$_2$O$_3$, respectively, with values of 8.7 eV and 6.9 eV, respectively. These are consistent with previous reported values.\(^{38-30}\)

### Tables

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<tr>
<th>Aluminum Concentration</th>
<th>Reference $(Al,Ga)<em>{2}O</em>{3}$</th>
<th>Reference SiO$_2$</th>
<th>Thin SiO$<em>2$ on $(Al,Ga)</em>{2}O_{3}$</th>
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<td>Core - VBM</td>
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<th>Core - VBM</th>
<th>Core - VBM</th>
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Table I. Summary of the measured reference and heterostructure peaks for SiO$_2$ on $(Al,Ga)_{2}O_{3}$ (eV).

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<tr>
<th>Aluminum Concentration</th>
<th>Reference $(Al,Ga)<em>{2}O</em>{3}$</th>
<th>Reference Al$_2$O$_3$</th>
<th>Thin Al$<em>2$O$<em>3$ on $(Al,Ga)</em>{2}O</em>{3}$</th>
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<td>VBM</td>
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Table II. Summary of the measured reference and heterostructure peaks for Al$_2$O$_3$ on $(Al,Ga)_{2}O_{3}$ (eV).
Figure 7. High resolution XPS spectra for the (a-b.) \((Al_{x}Ga_{1-x})_2O_3\) to SiO\(_2\) core delta regions and the (c-d.) \((Al_{x}Ga_{1-x})_2O_3\) to Al\(_2\)O\(_3\) core delta regions. The intensity is in arbitrary units (a.u.).

values were determined by linear extrapolation of the leading edge to the baseline of the valence band spectra. The error bars in the different binding energies were combined in a root sum square relationship to determine the overall error bars in the valence band offsets.\(^{30}\)

The valence band offsets for SiO\(_2\) were 1.25 ± 0.20 eV for \(\beta-(Al_{0.2}Ga_{0.8})_2O_3\), 1.3 ± 0.20 eV for \((Al_{0.35}Ga_{0.65})_2O_3\), 1.35 ± 0.20 eV for \((Al_{0.5}Ga_{0.5})_2O\) and 1.4 ± 0.20 eV for \((Al_{0.65}Ga_{0.35})_2O_3\). Based on the measured bandgap of this dielectric, the conduction band offsets are then 2.35 eV (\(x = 0.2\)), 2.20 eV (\(x = 0.35\)), 1.7 eV (\(x = 0.4\)) and 1.4 eV (\(x = 0.65\)). SiO\(_2\) therefore provides excellent confinement of electrons in \((Al_{x}Ga_{1-x})_2O_3\) samples over the practical range of Al contents achievable. The SiO\(_2/\beta-(Al_{x}Ga_{1-x})_2O_3\) band alignment remained type I across the entire composition range examined here, as shown in the schematic of Figure 8. Note that our valence band offsets are 0.10-0.45 eV different (both larger or smaller, depending on composition) than reported by Feng et al.\(^{24,25}\) for similar deposition conditions for the SiO\(_2\) on \((Al_{x}Ga_{1-x})_2O_3\) of comparable compositions to those used here. There are no obvious signs of metal contamination in the reported XPS survey spectra, so this gives an idea of the inherent accuracy of comparing valence band offsets values in the literature for the same dielectric/semiconductor systems.

Figure 8. Band diagrams for the SiO\(_2/(Al_{x}Ga_{1-x})_2O_3\) heterostructure in which the SiO\(_2\) was deposited by ALD.

\[ \begin{array}{c|c|c|c|c}
\text{SiO}_2 & \text{\((Al_{x}Ga_{1-x})_2O_3\)} & \text{\(x = 0.2\)} & \text{\(x = 0.35\)} & \text{\(x = 0.5\)} & \text{\(x = 0.65\)} \\
\hline
2.35 eV & 2.05 eV & 1.70 eV & 1.40 eV \\
 \end{array} \]
The valence band offsets for $\text{Al}_2\text{O}_3$ are in the range 0.23-0.33 eV for the same range of Al contents in $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$. The CCS-PLD technique provides an effective pathway to producing a wide range of compositions for study of band alignments.

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