I. INTRODUCTION

β-Ga2O3 is a wide bandgap semiconductor (~4.9 eV) with properties suited to power electronics, truly solar-blind UV detection, and extreme environment applications.1–14 The β monoclinic polymorph of Ga2O3 is the most prominent of the five phases of this material, and crystals up to 4 in. in diameter are commercially available. Ga2O3 has the potential to surpass GaN (bandgap 3.4 eV) for extreme environment operation. Kim et al.15 have already shown operation of a nanobelt field effect transistor (FET) device from room temperature to 250 °C with no hysteresis of the device, and higher current and transconductance at elevated temperatures. Promising device performance has been reported for rectifiers, transistors, and solar-blind photodetectors on bulk, epitaxial and thin flakes of β-Ga2O3.6–13,16–21 Ga2O3 has a theoretical field breakdown of 8 MV/cm, with experimental values reaching 3.8 MV/cm, surpassing the theoretical limit of GaN at 3.3 MV/cm. The current record of reverse breakdown of a vertical Schottky diode is 2300 V,22 and the highest reported breakdown for a nonplanar device channel was set using a Ga2O3 FinFET at 612 V using Al2O3 as the gate dielectric.16,18 The only disadvantage in Ga2O3’s material properties is the relatively low thermal conductivity.23

Across all these applications, understanding and properly selecting a gate dielectric either in metal-oxide-semiconductor field effect transistor (MOSFET), metal-insulator-semiconductor field effect transistor, or diode design is required. With selection of a gate dielectric, generally at least a 1 eV difference between the insulating material on the gated area and the channel semiconductor is preferred for performance, as that difference will provide a sufficient energy barrier to hole and electron leakage current.2,3,6 The majority of published MOSFET work on Ga2O3 has typically been either atomic layer deposited (ALD) Al2O3 or HfO2 or ALD and plasma enhanced chemical vapor deposited SiO2 and Al2O3 as the gate dielectrics, as they provide sufficient conduction band difference, reported from 1.5 to 3.1 eV.23–36

Additional bandgap tunability can be achieved through incorporation of Al into β-Ga2O3, leading to β-Al1-xGa1-xO3 monoclinic phase alloys with the bandgap tuned from 4.8 to 6 eV.16–24 This enables heterostructure designs such as modulation-doped electron channels, quantum wells, and superlattices.16–21 A number of reports of modulation-doped field effect transistors using β-Al1-xGa1-xO3/Ga2O3 heterostructures show effective quantum confinement of electrons at the interface.16–21 These devices require robust gate dielectrics. While band offsets for SiO2 on (AlxGa1−x)2O3 grown by pulsed laser deposition (PLD) have been reported for various values of x,25 it is of interest to get results on molecular beam epitaxy (MBE)-grown layers, which should have better prospects of producing device-quality material.

There is typically variability reported in the literature for both valence and conduction band offsets on oxides such as indium gallium zinc oxide, Ga2O3, and (Al1-xGa1-x)2O3 due to various effects,37,38 which may include metal contamination in the deposited dielectric (especially in sputtered films), interface disorder, differences in dielectric composition as a result of different deposition methods or precursors, carbon/hydrogen contamination, annealing, stress/strain, and the type of surface termination. In some cases, these result in differences in the bandgap of the dielectric and thus affect the conduction band offset. Generally, the valence band offset is measured directly, and the conduction band offset is calculated from the difference between that and the bandgaps.39,40 However, the valence band offset can also be affected by most of these same issues. The use of ALD deposited dielectrics minimizes most of these effects and provides a more controlled method for making the heterostructure samples for determining the band alignment.

In this paper, we report on the determination of the band alignment in the SiO2/(Al0.14Ga0.86)2O3 heterostructure, in which the SiO2 was deposited by ALD. We employ XPS to...
determine the valence band offsets and by measuring the respective bandgaps of the SiO$_2$ (8.7 eV) and β-(Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ (5.0 eV), we were able to determine the conduction band offset in the heterostructures and determine the band alignment.

II. EXPERIMENT

The SiO$_2$ was deposited by ALD on (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$/Ga$_2$O$_3$ structures and also quartz substrates. The latter were used for dielectric constant and composition measurements. Both thick (200 nm) and thin (1.5 nm) layers of the dielectrics were deposited to be able to measure both bandgaps and core levels on the β-(Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$. For substrate cleaning predetermination, the following rinse sequence was employed: acetone, isopropyl alcohol, N$_2$ dry, and cleaning predeposition, the following rinse sequence was finally room environment. Potential contamination of deposited ozone exposure for 15 min. After substrate cleaning, samples were directly loaded into the ALD system within a clean room environment. Potential contamination of deposited films can influence the bandgap and offset of the dielectric material. To minimize this problem, the SiO$_2$ layers were deposited at 200 °C in a Cambridge Nano Fiji 200, a remote plasma atomic layer deposition tool, using an inductively coupled plasma source at 300 W. Atomic layer deposition is an effective method for band offset studies, because it can be utilized with a remote plasma to reduce contamination effects and also provides minimal disruption to the heterointerface due to reduced ion damage from using a remote source. The SiO$_2$ layers were deposited using precursors of tris (dimethylamino) silane and O$_2$ at a deposition rate of 0.63 Å/cycle. After ALD deposition, the samples were transferred directly to the XPS system. These films were deposited onto epi (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ that was grown by molecular beam epitaxy. These aluminum gallium oxide layers were doped with Si to produce a n-type carrier density of 10$^{17}$ cm$^{-3}$ and were 55 nm thick. This represents an advance in n-type doping capability because Si source material can suffer oxidation during growth unless precautions are taken in terms of shuttering the Si source and preheating prior to actual opening of the shutter to avoid this issue. The carrier concentration was determined by electrochemical capacitance-voltage profiling at a frequency of 740 Hz on calibration samples and the composition was determined by x-ray diffraction on these same samples. The latter composition was confirmed by ion microprobe data. These epitaxial layers were grown on top of Sn-doped (6.3 × 10$^{18}$ cm$^{-3}$) bulk β-phase Ga$_2$O$_3$ single-crystal substrates (500 μm thick) with (010) surface orientation (Tamura Corporation, Japan) grown by the edge-defined film-fed growth method. The heterostructure sample is shown schematically in Fig. 1.

To obtain the valence band offsets, XPS survey scans were performed to determine the chemical state of the SiO$_2$ and β-(Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ and identify peaks for high resolution analysis.$^{39,40}$ An ULVAC PHI XPS with an aluminum x-ray source (energy 1486.6 eV) with source power 300 W was used, with an analysis area of 20 μm in diameter, a take-off angle of 50°, and an acceptance angle of ±7°. The electron pass energy was 23.5 eV for the high resolution scans and 93.5 eV for the survey scans. The approximate escape depth (3λ sin θ) of the electrons was 80 Å. All of the peaks are well defined in this system.

Charge compensation was performed using an electron flood gun. The charge compensation flood gun is often not sufficient at eliminating all surface charge, and additional corrections must be performed. Using the known position of the adventitious carbon (C–C) line in the C 1s spectra at 284.8 eV, charge correction was performed. During the measurements, the samples and electron analyzers were electrically grounded to provide a common reference Fermi level. Differential charging is a concern for semiconductor band offset measurements$^{31-50}$ and while use of an electron flood gun does not guarantee that differential charging is not present, our experience with oxides on conducting substrates has been that the differential charging is minimized with the use of an electron gun. Calibrations with and without the gun verified that was the case. This procedure has been described in detail previously.$^{38}$

Reflection electron energy loss spectroscopy (REELS) was employed to measure the bandgap of the SiO$_2$. This technique works well for the wider gap materials. REELS is capable of analyzing electronic and optical properties of ultrathin gate oxide materials since the low-energy-loss region reflects the valence and conduction band structures.$^{40,41}$ As electrons are reflected off the surface, energy is lost at energy bands related to excitation of the substrate’s electrons. The excitation from the valence band to conduction band is the lowest energy loss possible by an incident electron.
electron excluding elastic reflection with no energy loss. By taking a linear fit to the leading plasmon peak and finding its zero energy with the background, a direct measurement of valence to conduction band energy is made. REELS spectra were obtained using a 1 kV electron beam and the hemispherical electron analyzer.

III. RESULTS AND DISCUSSION

Figure 2 shows the stacked XPS survey scans of thick (200 nm) SiO₂, 1.5 nm ALD SiO₂ on β-(Al₀.₁₄Ga₀.₈₆)₂O₃, and an (Al₀.₁₄Ga₀.₈₆)₂O₃ reference sample. The spectra are free from contaminants and consistent with past published XPS data on these materials. To the detection limit of XPS, there were no metallic contaminants in the films whose oxides might lower the overall bandgap of the dielectrics and thus affect the band alignment. Carbon contamination was minimally present in the thick SiO₂ and 1.5 nm SiO₂ samples which was potentially introduced during the ALD process. The (AlGa)₂O₃ reference samples is free from carbon contamination due to being loaded into the XPS system directly after the sample cleaning sequence.

The valence band maximum (VBM) was determined by linearly fitting the leading edge of the valence band and the flat energy distribution from the XPS measurements, and finding the intersection of these two lines, as shown in Fig. 3 for (a) the thick SiO₂, and (b) the (Al₀.₁₄Ga₀.₈₆)₂O₃. The VBM were measured to be 3.0 ± 0.2 eV for β-(Al₀.₁₄Ga₀.₈₆)₂O₃ and 4.8 ± 0.4 eV for the SiO₂.

The measured band gap for the SiO₂ was 8.7 ± 0.4 eV from the REELS data of Fig. 4(a). As shown in Fig. 4(b), the bandgap of the β-(Al₀.₁₄Ga₀.₈₆)₂O₃ was determined to be 5.0 ± 0.3 eV, determined from the onset of the energy loss spectrum. This was used since REELS was not as accurate on the thin layers used here. We should also point out that a similar analysis on the SiO₂ produced a similar bandgap to the REELS result. The difference in bandgaps between SiO₂ and β-Ga₂O₃ is therefore 3.7 eV. The work of Krueger et al. determined the compositional dependence of bandgap in Al₁ₓGaₙ₋ₓO as a linear dependence on Al content, as

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

![Fig. 3. XPS spectra of core levels to VBM for (a) ALD thick film SiO₂ and (b) reference (Al₀.₁₄Ga₀.₈₆)₂O₃. The intensity is in arbitrary units (a.u.).](image)

![Fig. 4. Bandgap of (a) SiO₂ and (b) (Al₀.₁₄Ga₀.₈₆)₂O₃ determined by reflection electron energy loss spectra and the onset of energy loss spectrum, respectively. The intensities are in arbitrary units (a.u.).](image)
This would lead to a value of 5.01 eV, consistent with our result. Their data are based on XPS analyses for polycrystalline samples and can be considered as an averaged standard. Wakabayashi et al. reported a more pronounced bowing behavior for the compositional dependence of bandgap in \((\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3\) alloys, with systematically lower bandgaps at each composition, including pure \(\text{Ga}_2\text{O}_3\). They suggested this was due to strain in their layers as well as dependence on measurement technique and geometry. Using the equation below, theoretical calculations suggest a dependence of \(E_g = \left(\frac{1}{C_0}\right)E_{g[\text{Ga}_2\text{O}_3]} + xE_{g[\text{SiO}_2]} - bx\left(\frac{1}{C_0}\right)\)

where \(b\) is the bowing parameter with values between 1.78 and 1.87 eV. For our sample with \(x = 0.14\), this would lead to a bandgap of 5.14 eV.

To determine the band alignment and valence and conduction band offsets, we examined the core level spectra for the samples. Valence band offset is predominantly determined via x-ray photoelectron spectroscopy (XPS) using a method detailed by Kraut et al. This method relies on precise measurement of a core level and the valence band edge for each material investigated and measurement in the shift of the core levels when the two materials have formed the heterojunction. Previously, Kraut et al. used a valence band density of states fitting for precise measurement of the valence band edge; however, using a linear extrapolation method has been demonstrated to be just as accurate and less intensive. The equation used to calculate the offset is

\[
\Delta E_V = \left(\frac{E_{1\text{core}}}{E_{1\text{VBM}}} - \frac{E_{2\text{core}}}{E_{2\text{VBM}}}\right)\left(\frac{E_{1\text{core}}}{E_{2\text{core}}}\right) - \left(\frac{E_{1\text{core}} - E_{2\text{core}}}{E_{1\text{VBM}} - E_{2\text{VBM}}}\right).
\]

Selection of a core level which is well defined and as close as possible in energy to the heterojunction is preferred, because the offsets are small compared to the core level energy and more deviation is expected at higher core level energies.

High resolution XPS spectra of the VBM-core delta region are shown in Fig. 5(a) for the \(\beta-(\text{Al}_{0.14}\text{Ga}_{0.86})_2\text{O}_3\) and thick ALD SiO₂ (b) samples. These were used to determine the selected core level peak positions. Figure 6 shows the XPS spectra for the \(\beta-(\text{Al}_{0.14}\text{Ga}_{0.86})_2\text{O}_3\) to SiO₂ core delta

<table>
<thead>
<tr>
<th>Reference (AlGa)₂O₃</th>
<th>Reference SiO₂</th>
<th>Thin SiO₂ on (AlGa)₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core level VBM</td>
<td>Core level peak</td>
<td>Core—VBM Core level VBM</td>
</tr>
<tr>
<td>VBM</td>
<td>Core—VBM</td>
<td>1117.60</td>
</tr>
<tr>
<td>Si 2p</td>
<td>4.80</td>
<td>103.40</td>
</tr>
<tr>
<td>Δ core level Ga 2p½ — Si 2p</td>
<td>1014.40</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table I. Summary of measured core levels in these experiments (eV).
regions of the heterostructure samples. These values are summarized in Table I and were then used to calculate $\Delta E_v$.

Figure 7 shows the band alignment of the SiO$_2$/β-(Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ heterostructure. This is a nested, type I system with a valence band offset of 1.60 ± 0.40 eV and conduction band offset of 2.10 ± 0.08 eV for the SiO$_2$/β-Ga$_2$O$_3$ system using the relationship

$$\Delta E_C = E_{g}^{SiO_2} - E_{g}^{AlGaO} - \Delta E_V, \text{ i.e., } \Delta E_C$$

$$= 8.7 \text{ eV} - 5.0 \text{ eV} - 1.60 \text{ eV} = 2.10 \text{ eV}.$$  

The valence band offset is large enough to provide effective hole confinement, and the conduction band offset is well above the desirable value of 1 eV for good electron confinement, providing a strong resistance to electron transport even at high temperature device operation. Additional dielectrics should be examined, especially as higher Al content β-(Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ is developed for heterostructure transistors.

Feng et al. reported band alignments of SiO$_2$/β-(Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ films grown by pulsed laser deposition over the composition range 0 ≤ x ≤ 0.49 and the dielectric deposited by ALD. They also found type I alignments, with similar conduction offsets and smaller valence offsets at our particular Al content. Their conduction band offsets increased from 1.5 to 2.1 eV, respectively, over this composition range while the valence band offsets decreased from 2.2 to 0.9 eV. For some dielectric/semiconductor systems, energy band alignment variations more than 1 eV have reported depending on the interface preparation. The interface preparation method influences the band alignment due to the presence of high defect concentrations in the materials and a cation effect that will increase the VBM. These differences are usually seen for the same heterostructure when comparing different deposition methods, i.e., sputtering is more prone to creating interfacial disorder and contributing metallic contamination that affects the bandgap of the dielectric. When comparing the results shown in this study (ALD SiO$_2$) to Feng’s published work (PLD SiO$_2$), similar offset trends were achieved. Therefore, no significant band alignment differences were noted when comparing SiO$_2$ films deposited using ALD or PLD. To conclude if growth method impacts the SiO$_2$/β-Ga$_2$O$_3$ interface, additional studies should be performed using the same Al concentration and substrate growth method. Furthermore, the SiO$_2$/β-(Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ alignment presented in this work is reasonable when compared to previous reports of SiO$_2$ on undoped Ga$_2$O$_3$.

IV. SUMMARY AND CONCLUSIONS

The band alignment at SiO$_2$/β-(Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ heterojunctions was obtained from XPS measurements and found to be a nested gap (type I) band offset. The valence band offset was 1.60 ± 0.40 eV and the conduction band offset was 2.10 ± 0.08 eV. The valence band offset is sufficient for hole confinement, while the conduction band offset provides excellent restriction to electron transport. A comparison of the literature to date on band offsets for dielectrics on β-(Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ shows no significant variations between material deposited by pulsed laser deposition compared to the MBE-grown samples used here.

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