Band Offsets of (100) β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 Heterointerfaces Grown via MOCVD

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The valance and conduction band offsets at (100) β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 heterointerfaces with increasing Al composition are determined via X-ray photoelectron spectroscopy. The (100) β-$(Al_xGa_{1-x})_2O_3$ thin films with Al composition of $0.10 < x < 0.52$ are grown on (100) β-Ga_2O_3 substrates by metalorganic chemical vapor deposition method. By examining the onset of inelastic energy loss in core-level atomic spectra, the bandgaps of β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ alloys with different Al compositions are measured from 4.83 ± 0.12 eV (x = 0) to 5.85 ± 0.08 eV (x = 0.52). The valance band offsets are determined as -0.06 ± 0.06 eV (x = 0.10), -0.11 ± 0.06 eV (x = 0.33) and -0.19 ± 0.06 eV (x = 0.52). The conduction band offsets of 0.34 ± 0.17 eV (x = 0.10), 0.62 ± 0.17 eV (x = 0.33) and 1.21 ± 0.16 eV (x = 0.52) are determined from the extracted band gaps of β-$(Al_xGa_{1-x})_2O_3$ alloys. The determined band alignments at β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces reveal the formation of type-II (staggered gap) heterojunction for all Al compositions investigated. The bowing parameters obtained from the quadratic fitting of both conduction band minimum and valance band maximum values are estimated to be 1.25 eV and 0.005 eV, respectively.

Keywords: Ultrawide bandgap, metalorganic chemical vapor deposition (MOCVD), band offsets, X-ray photoelectron spectroscopy

β-Ga_2O_3 has gained great attention due to its ultra-wide bandgap energy (~4.8 eV) promising for power electronic and optoelectronic applications [1-21]. Recently, the interest in bandgap engineering of Ga_2O_3 through Al alloying has been increased significantly as many applications require the formation of $(Al_xGa_{1-x})_2O_3/Ga_2O_3$ heterostructures. Due to the feasibility of tuning the bandgap from ~4.8 eV (β-Ga_2O_3) to 8.82 eV (α-Al_2O_3) [22], $(Al_xGa_{1-x})_2O_3$ can take advantage of its larger bandgap energy to achieve higher critical electric field strength. Furthermore, alloying Ga_2O_3 with Al_2O_3 can open-up the possibility for realizing high-performance lateral devices based on $(Al_xGa_{1-x})_2O_3/Ga_2O_3$ heterostructures through device scaling [23-25].

Recent efforts on the growth of β-$(Al_xGa_{1-x})_2O_3$ alloys by different growth techniques including metal organic chemical vapor deposition (MOCVD) [26-30], molecular beam epitaxy (MBE) [31-33], and pulsed-laser deposition (PLD) [34] indicate the possibility to achieve high quality films on β-Ga_2O_3 substrates with different orientations such as (010) [26-28,31,33], (100) [29,32,34] and $(\bar{2}01)$ [30]. While incorporating high Al composition in pure β-phase $(Al_xGa_{1-x})_2O_3$ is found to be challenging on (010) oriented β-Ga_2O_3 substrates ($x < 27\%$) due to domain rotation and phase segregation [28], the use of other orientation of β-Ga_2O_3 substrates such as (100) [29,32] and $(\bar{2}01)$ [30] for β-$(Al_xGa_{1-x})_2O_3$ epitaxy shows a great promise to achieve higher Al compositions ($x > \sim 50\%$) in pure β-phase. In order to improve the two-dimensional electron density in β-$(Al_xGa_{1-x})_2O_3/Ga_2O_3$ interface and for better carrier confinement in β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 based MODFET devices, higher Al incorporation in β-$(Al_xGa_{1-x})_2O_3$ barrier layer is essential. In addition, accurate estimation of the band alignment of β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces is also critical for device design and quantitative analysis of the carrier confinement at the interface.

For designing β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 based heterojunction devices, knowledge of conduction band minimum and valance band maximum energy discontinuities between β-$(Al_xGa_{1-x})_2O_3$ and its adjacent β-Ga_2O_3 is crucial for predicting the transport properties and the electrostatic potential of the interface. Compared to other methods, x-ray photoelectron spectroscopy (XPS) has been widely used as a direct and non-destructive technique to determine the valance band offsets of the heterojunctions [35-37]. Recently, by utilizing XPS, several studies have been conducted on the measurement of band offsets between insulating oxides and β-Ga_2O_3, such as PLD γ-Al_2O_3/β-Ga_2O_3 [38], SiO_2/β-Ga_2O_3 [39], and ALD Al_2O_3/β-Ga_2O_3 [40, 41]. Separately, a valence band offset of 0.07 ± 0.20 eV (type I alignment) for ALD Al_2O_3 on $(\bar{2}01)$ β-Ga_2O_3, and -0.86 ± 0.25 eV (type II alignment) for sputtered Al_2O_3 were reported [42]. In addition to the band offset measurements at insulating oxides and β-Ga_2O_3 interfaces, there are reports on band offsets of SiO_2 or HfO_2 on β-$(Al_xGa_{1-x})_2O_3$ [43-46].

Experimental demonstration of the band alignments at β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces are still limited due to the unavailability of high quality β-$(Al_xGa_{1-x})_2O_3$ growth. A recent study on a PLD β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interface (x = 37%) was determined to be a type I band alignment with conduction and valence band offsets of 0.52 ± 0.02 eV and 0.13 ± 0.07 eV, respectively [34]. However, theoretical studies based on density functional theory (DFT) revealed a type II band alignment [22, 47], with a valence-band offset of 0.33 eV [47] (0.37 eV [22]) and a conduction-band offset of 2.67 eV [47] (2.74 eV [22]). The wide spread of the experimentally reported band offset values and the deviation from the theoretically predicted band offset values can be a result of the low crystalline quality of the overlayers including interfacial disorder and the lack of interfacial abruptness [48, 49], rough surface morphology, carbon/hydrogen contamination, surface termination etc. Therefore, for the accurate measurement of band offsets at β-$(Al_xGa_{1-}$

$_x)_2O_3/\beta$-Ga_2O_3, high quality epifilms with abrupt interfaces and smooth surface morphology are needed.

In this letter, we report the valance and conduction band offsets between MOCVD grown high quality (100) β-$(Al_xGa_{1-x})_2O_3$ and β-Ga_2O_3 interfaces with Al compositions up to $x \leq 0.52$. The band gap energies and the valance band offsets for 10%, 33% and 52% Al compositions are determined via XPS. Using the band gap energies and the valance band offsets, the conduction band offsets are extracted and are found to be consistent with the theoretically predicted band offset values. As there are deviations in the previous experimental reports from theoretically predicted band offset values, this report seeks to fill the fundamental gap with respect to the band offsets in β-$(Al_xGa_{1-x})_2O_3/\beta$-$Ga_2O_3$ interfaces with the evolution of Al compositions. In this study, (100) β-$(Al_xGa_{1-x})_2O_3$ thin films were grown via MOCVD on Fe doped semi-insulating (100) β-Ga_2O_3 substrates (commercially acquired from Novel Crystal Technology, Inc.). Triethylgallium (TEGa), and Trimethylaluminum (TMAl) were used as Ga and Al precursors, respectively. Pure O_2 was used as the O precursor and argon (Ar) was used as the carrier gas. The chamber pressure was varied between 50 and 80 torr. The growth temperature was kept at 880 °C. [TMAl]/[TEGa+TMAl] molar flow rate ratio was tuned from 2.35% to 22.21%. As part of the substrate preparation, prior to the epitaxial growth, β-Ga_2O_3 substrates were treated with high temperature in-situ annealing for 10 minutes at 920°C under O_2 atmosphere for removing the potential contamination from the substrate surface.

To confirm the Al compositions and to determine the band gaps and the band offsets, chemical bonding states were studied by utilizing XPS. XPS measurements were performed using a Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromatized Al Kα x-ray source (E_{photon} = 1486.6 eV) with an energy resolution of 0.1 eV. The bandgap energies were calculated by

measuring the onset of inelastic loss spectra relative to the O 1s core level peaks. The crystalline quality and the Al compositions of the films were evaluated by x-ray diffraction spectra (XRD, Bruker D8 Discover). Atomic force microscopy (AFM, Bruker ICON) and a field emission scanning electron microscopy (FESEM, FEI Helios 600) were used to evaluate the surface morphology and roughness. High angle annular dark field (HAADF) STEM images were obtained by using a Thermo Fisher Scientific Themis-Z scanning transmission electron microscope operated at 200 kV.

A series of samples with targeted 10%, 33% and 52% Al compositions were grown by varying the [TMAl]/[TMAl+TEGa] molar flow ratio. Figures S1 (a)-(c) in the supplementary material show the schematics of the samples that were used to determine the band alignment at β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces by using XPS: (a) 150 nm thick β-Ga_2O_3 film grown on (100) β-Ga_2O_3 substrate, (b) 50 nm thick β-$(Al_xGa_{1-x})_2O_3$ (x = 10%, 33% and 52%) film grown on top of 65 nm thick (100) β-Ga_2O_3 buffer layer, and (c) 2 nm thick β-$(Al_xGa_{1-x})_2O_3$ (x = 10%, 33% and 52%) layer grown on top of 65 nm thick (100) β-Ga_2O_3 buffer layer and (100) β-Ga_2O_3 substrates.

As XPS measurement is surface sensitive, the surface roughness of β-$(Al_xGa_{1-x})_2O_3$ and β-Ga_2O_3 films can affect the data accuracy. The smooth and uniform surface can help to access all electronic states intrinsic to the interface. To investigate the surface features and to estimate the surface roughness, AFM and SEM imaging for the films with different Al compositions were performed as shown in Figures 1(a)-(d) and in Figures S2 of the supplementary materials, respectively. While PLD [34] growth of (100) β-$(Al_xGa_{1-x})_2O_3$ films were demonstrated with flat surface morphology by using the repeating alternate ablation technique, both MOCVD [26,29,30] and MBE [31,32] growth of (100) [29,32], $(\bar{2}01)$ [30] and (010) [26,31] oriented β-$(Al_xGa_{1-x})_2O_3$ films showed obvious changes in the surface morphology as the Al composition changes. The

changes in the Al adatoms diffusivity on the growth surface with different Al compositions can lead to the surface morphological changes. Although granular surface morphology was observed for the samples with different Al compositions, the surface root mean square (RMS) roughness of an area of 3 x 3 μm^2 for both β-Ga_2O_3 (150 nm thick) and β-$(Al_xGa_{1-x})_2O_3$ (50 nm thick) films were varied between 0.50 nm to 0.76 nm, indicating uniform and smooth surface morphology. The crystalline quality of β-$(Al_xGa_{1-x})_2O_3$ films with different Al compositions was also investigated by the XRD measurement as shown in Fig. S3 in the supplementary material. The full-width at half-maximum (FWHM) of the ω rocking curve was measured as 85, 95 and 111 arcsec for the (400) reflection of β-$(Al_xGa_{1-x})_2O_3$ films with 10%, 33% and 52% Al compositions, respectively. The narrow rocking curves with smaller FWHM values also indicate the growth of high-quality epitaxial films on (100) β-Ga_2O_3 substrates.

In addition, the quality of β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 growth, especially at the interface, is critical for accurate measurement of band offsets. To investigate the interfacial abruptness, β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 with 10%, 33%, and 52% Al compositions were investigated using high resolution STEM imaging and energy-dispersive x-ray spectroscopy (EDS). Figures 2(a)-(c) show the atomic resolution HAADF STEM images for $[001]_m$ β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces with film compositions of 10%, 33%, and 52% Al. The undisturbed β-phase structure and the sharp contrast between the β-$(Al_xGa_{1-x})_2O_3$ epi-film (dark) and the β-Ga_2O_3 layer (bright) reveal high quality interfaces for each sample. EDS performed throughout the entirety of the films, shown in Figs. 3(a)-(l), also demonstrates the abrupt interfaces. Additionally, EDS was used to estimate the Al distribution across the grown films. Generally, the samples with 10% and 52% Al compositions reveal uniform distribution of Al throughout the films. EDS from the 33% Al film [Figs. 3(e)-(h)] shows fluctuation of Al compositions throughout the film. The average Al compositions in all

films show a good agreement with those extracted from XRD and XPS measurements, as presented later.

The recent theoretical DFT calculation on the critical thickness of $(Al_xGa_{1-x})_2O_3$ alloys grown on Ga_2O_3 substrates shows higher critical thickness for (100) β-$(Al_xGa_{1-x})_2O_3$ films than other orientations such as (010) and (001) [50]. Considering different critical thicknesses for different Al compositions, the strain in (100) β-$(Al_xGa_{1-x})_2O_3$ films with different Al compositions can be different. As there exists no ideal $(Al_xGa_{1-x})_2O_3/Ga_2O_3$ interfaces without strain, this report investigates the effect on the experimental band offset values of (100) $(Al_xGa_{1-x})_2O_3/Ga_2O_3$ interface with different Al compositions. Although extended defects such as twin boundaries [29] and slight Al and Ga diffusion at the interface were observed in the (100) oriented β-$(Al_xGa_{1-x})_2O_3$ films, the lower surface roughnesses with sharp interfaces indicate the decent epitaxial growth of (100) β-$(Al_xGa_{1-x})_2O_3$ films on β-Ga_2O_3 substrates, which are essential for the extraction of the band offsets by using surface sensitive XPS.

The elemental compositions of 50 nm thick β-$(Al_xGa_{1-x})_2O_3$ films were also estimated by utilizing the XPS technique. Due to the large sampling depth of other techniques such as Rutherford backscattering or energy-dispersive X-ray spectroscopy (EDX), the reliable determination of the elemental compositions for thin epi-films is nontrivial. As the sampling depth of XPS techniques is only a couple of nanometers, it allows an accurate determination of the elemental compositions of the films. The Al compositions are determined by analyzing the area of Ga 3s and Al 2s core levels with their respective sensitivity factors ($S_{Ga\ 3s}$ = 1.13 and $S_{Ga\ 2s}$ = 0.753) after applying the Shirley background subtraction. The corresponding survey spectra for β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ samples with different Al compositions and Ga 3s and Al 2s core level spectra are shown in the Figures S4 and S5 of the supplementary materials, respectively. No metallic

contaminants other than Ga, Al, C and O were observed in the survey spectra, indicating high crystalline quality epi-films. The Al compositions estimated by using Ga 3s and Al 2s core level spectra as listed in Table S1 of the supplementary materials agrees well with the Al compositions determined by X-ray diffraction (XRD) spectra in Figure S3 of the supplementary material.

In order to estimate the bandgap energies of β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ films, the inelastic energy loss spectrum of the O 1s core level XPS peak was utilized. The onset of the inelastic loss spectrum at lower kinetic energy (higher binding energy) relative to the core level peak corresponds to the bandgap energy [51]. Figures 4 (a)-(d) show the O 1s core level spectrum of β-Ga_2O_3 film and β-$(Al_xGa_{1-x})_2O_3$ films with x = 10%, 33% and 52%, respectively. The bandgaps estimated by measuring the onset of energy loss peaks are 4.83 ± 0.12 eV, 5.11 ± 0.10 eV, 5.34 ± 0.10 eV and 5.85 ± 0.08 eV for x = 0%, 10%, 33% and 52%, respectively, as listed in Table 1 and in Fig. S6 of the supplementary materials. The experimental bandgap energies measured at different Al composition samples are in a good agreement with the DFT calculations. The bowing parameter (b) obtained from the quadratic fitting of the experimentally observed bandgap values is 1.25 eV. This experimental value agrees well with the theoretically calculated value of b = 0.93 eV (indirect) [1.37 eV (direct)] [52].

By utilizing XPS, the valance band offsets (ΔE_v) at β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 heterointerfaces with different Al compositions were calculated by using Ga $2p_{3/2}$ and Al 2p core level spectra and the valance-band (VB) spectra of β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ films. Figures 5(a)-(d) show the valance band spectra and Ga $2p_{3/2}$ and Al 2p core-level spectra for β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ films with 52%, 33% and 10% Al compositions, respectively. The position of the VB onsets for each sample is estimated through a linear extrapolation of the leading edge of the valence band spectra to the background as shown in the cross-over points in Figures 5(a)-(d). The Ga $2p_{3/2}$ and

Al 2p core level positions for β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ are determined by fitting with a combination of Gaussian and Lorentzian line shapes after applying Shirley background subtraction.

XPS is well-established to determine the band discontinuities at the heterojunction interface. Although ΔE_v at the interface of two materials can be directly determined by utilizing the difference between their VB onsets, for more accurate determination of the valance band offsets between β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ with different Al compositions, we have employed the Kraut's method [36], which has been reported by many reports [34,38,42] to determine the valance band offsets. The details on the valence and conduction band offsets extraction are included in the supplementary materials.

The binding energy difference ($E^{GaO}_{Ga\ 2p_{3/2}}$ - E^{GaO}_{VBM}) between Ga $2p_{3/2}$ core level and the VB onsets for β-Ga_2O_3 (GaO) is estimated to be 1114.46 ± 0.04 eV as shown in Figure 5(a). For β-$(Al_xGa_{1-x})_2O_3$ (AlGaO) samples with 52%, 33% and 10% Al compositions, the binding energy differences ($E^{AlGaO}_{Al\ 2p}$ - E^{AlGaO}_{VBM}) between Al 2p and VB onsets are determined as 70.90 ± 0.04 eV (x = 10%), 71.02 ± 0.04 eV (x = 33%) and 70.99 ± 0.04 eV (x = 52%). For the $(Al_xGa_{1-x})_2O_3/Ga_2O_3$ (AlGaO/GaO) interface samples, the binding energy differences ($E^{AlGaO/GaO}_{Ga\ 2p_{3/2}}$ - $E^{AlGaO/GaO}_{Al\ 2p}$) between Ga $2p_{3/2}$ and Al 2p core levels are determined as 1043.61 ± 0.02 eV (x = 10%), 1043.55 ± 0.02 eV (x = 33%) and 1043.66 ± 0.02 eV (x = 52%) as represented in Figures 5(b)-(d). Using equation (S1), the valance band offsets (ΔE_v) between β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ films for 10%, 33% and 52% Al composition samples are determined as -0.06 ± 0.06 eV (x = 10%), -0.11 ± 0.06 eV (x = 33%) and -0.19 ± 0.06 eV (x = 52%). By utilizing the bandgap energies β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ films and the ΔE_v values obtained through equation (S1), the conduction band offsets

(ΔE_c) between β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ films are calculated as 0.34 ± 0.17 eV (x = 10%), 0.62 ± 0.17 eV (x = 33%) and 1.21 ± 0.16 eV (x = 52%) by using equation (S2). To verify the values of valance band and the conduction band offsets achieved, calculation based on the Al 2s core level energy is also carried out. Comparison of the values obtained by using both Al 2p and Al 2s with Ga $2p_{3/2}$ are summarized in Table 1, which shows consistent ΔE_v and ΔE_c values at different Al compositions. The valance band and the conduction band offset values extracted by using different core level XPS peaks match well with the theoretically predicted values [22, 47].

Based on the calculated bandgaps and the values of ΔE_v and ΔE_c, the band alignments at β-Ga_2O_3/β-$(Al_xGa_{1-x})_2O_3$ heterojunctions with different Al compositions are plotted in Figures 6(a), which indicate that the investigated β-Ga_2O_3/β-$(Al_xGa_{1-x})_2O_3$ interfaces have type II staggered band alignment which is in agreement with prediction by DFT calculations [22, 47]. While a recent report on the band offset measurement is demonstrated with a type-I band alignment between PLD grown (100) β-Ga_2O_3/β-$(Al_xGa_{1-x})_2O_3$ interfaces [34], our result shows a type-II band alignment. The differences from the previous report on the band offset values can be caused by the differences in the property of the epi-layers as the films are grown under different growth environments via different growth techniques. Figure 6(b) shows the valance band maximum (VBM) and conduction band minimum (CBM) positions for β-$(Al_xGa_{1-x})_2O_3$ as a function of the alloy concentration. The values at the VBM and CBM indicate the valance band and the conduction band offsets, respectively, calculated by considering the valance band edge of monoclinic β-Ga_2O_3 at 0 eV. The measured VBM and CBM values for different Al compositions are represented by black solid symbols. The blue solid lines represent the quadratic fit to the measured CBM and VBM values and the red dashed line is the computed CBM and VBM values for monoclinic structure as reported in ref [52]. Both VBM and CBM values increase as the Al composition increases. While the CBM

values increase largely as the Al content increases from 10% to 52%, there is only slight increase in VBM values with increasing Al compositions, which is expected as O 2p states dominate the VBM [22, 47]. The bowing parameter obtained from the quadratic fitting of both VBM and CBM values (as depicted by the blue solid lines) are estimated to be 0.005 eV and 1.25 eV, respectively.

In summary, via XPS measurements, the band gap energies as well as the valance and the conduction band offsets at (100) β-Ga_2O_3/β-$(Al_xGa_{1-x})_2O_3$ heterojunctions are determined over a wide Al composition range ($x \leq 0.52$). The band gaps are estimated to be varied between 4.83 ± 0.12 eV [β-Ga_2O_3] and 5.85 ± 0.08 eV [β-$(Al_{0.52}Ga_{0.48})_2O_3$]. β-$Ga_2O_3$ films form a type II heterostructure with β-$(Al_xGa_{1-x})_2O_3$ alloy for all investigated compositions with the conduction band offsets up to 1.21 ± 0.16 eV ($x = 0.52$). The valance band offsets of up to -0.19 ± 0.06 eV ($x = 52\%$) are determined. A much weaker variations in the valance band offsets are observed as compared to the conduction band offsets. The bowing parameter for the valance band maximum and the conduction band minimum are determined as 0.005 eV and 1.25 eV, respectively. The demonstration of the bandgaps and the valance and the conduction band offsets at (100) β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces with the variation of alloy compositions would provide guidance for future device designs.

See the supplementary material for the equations of calculating the valence/conduction band offset, the schematic of the samples, the XPS survey spectra, XRD ω-2θ and ω-rocking curve scan and the Al composition calculations from Ga 3s and Al 2s core level spectra for β-$(Al_xGa_{1-x})_2O_3$ films with different Al compositions.

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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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Table Captions

Table 1. Summary of the Al compositions, the bandgap energies and the valance and conduction band offsets for (100) β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces, estimated by using valance band spectra, Ga $2p_{3/2}$, Al 2p and Al 2s core levels from XPS measurement. The valance and the conduction band offsets calculated by using both Al 2p and Al 2s core levels are listed for each Al composition sample, indicating the consistency in the measured values. The errors in the measured values are defined as the root-mean-square errors.

Figure Captions

Figure 1 AFM images (scan area: 3 x 3 μm^2) of (a) 150 nm thick (100) β-Ga_2O_3 films and 50 nm thick β-$(Al_xGa_{1-x})_2O_3$ alloys grown with Al compositions of (b) x = 10%, (c) x = 33% and (d) x = 52%.

Figure 2 Atomic resolution HAADF-STEM images of [001]m β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces (white-dashed line) with x = (a) 0.10, (b) 0.33, and (c) 0.52. β-$(Al_xGa_{1-x})_2O_3$ films were grown on top of a 65 nm thick β-Ga_2O_3 buffer layer on a (100) β-Ga_2O_3 substrate.

Figure 3 STEM-EDS for each β-$(Al_xGa_{1-x})_2O_3$ film. (a) HAADF image with corresponding (b) Ga and (c) Al EDS maps and (d) atomic fraction elemental profile (orange arrow in (a)) for x = 0.10. (e) HAADF image with corresponding (f) Ga and (g) Al EDS maps and (h) atomic fraction elemental profile (orange arrow in (e)) for x = 0.33. (i) HAADF image with corresponding (j) Ga and (k) Al EDS maps and (l) atomic fraction elemental (orange arrow in (i)) for x = 0.52.

Figure 4 The bandgap energies of (a) (100) β-Ga_2O_3 films and β-$(Al_xGa_{1-x})_2O_3$ alloys determined by the energy difference of O 1s core level peak and the onset of energy loss spectrum for (b) x = 10%, (c) x = 33%, and (d) x = 52%.

Figure 5 Ga $2p_{3/2}$ and Al 2p core-levels and valence band spectra of (a) β-Ga_2O_3 and (b-d) β-$(Al_xGa_{1-x})_2O_3$ alloys with different Al compositions. (b- i), (c- iii) and (d- v) represent the binding energy difference between Al 2p core levels and valance band onsets for 50 nm thick β-$(Al_xGa_{1-x})_2O_3$ alloys grown with Al compositions of (b) x = 52%, (c) x = 33%, and (d) x = 10%, respectively. The binding energy differences between Ga $2p_{3/2}$ and Al 2p core-levels for β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces are represented in (b- ii), (c- iv) and (d- vi) for x = 52%, 33% and 10% Al compositions, respectively.

Figure 6 (a) Band offsets at β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 interfaces for β-$(Al_xGa_{1-x})_2O_3$ alloys with Al compositions of 10%, 33% and 52%. The band gaps and the conduction and valance band

offsets value are represented in green, red and blue font colors, respectively. (b) The position of conduction band minimum (CBM) and valance band maximum (VBM) for β-$(Al_xGa_{1-x})_2O_3$ alloys as a function of Al compositions. The values at the VBM indicate valence-band offsets and values at the CBM indicate conduction-band offsets; by considering the valance band edge position of β-Ga_2O_3 at 0 eV. The black solid symbols represent the experimental values. Blue solid lines are the quadratic fitting of the measured CBM and VBM values and the red dashed lines represent the theoretically predicted CBM and VBM positions from ref [52].

Table 1

Al composition	Bandgap energy (eV)	Core levels (CL)	$E^{GaO}_{CL\ (GaO)} - E^{GaO}_{VBM}$ (eV)	$E^{AlGaO}_{CL\ (AlGaO)} - E^{AlGaO}_{VBM}$ (eV)	$E^{AlGaO/GaO}_{CL\ (GaO)} - E^{AlGaO/GaO}_{CL\ (AlGaO)}$ (eV)	Valance band offset ΔE_v (eV)	Conduction band offset ΔE_c (eV)
0%	4.83 ± 0.12	Ga $2p_{3/2}$	1114.46 ±0.04				
10%	5.11 ± 0.10	Al 2p		70.90±0.04	1043.61±0.02	-0.06 ± 0.06	0.34 ± 0.17
		Al 2s		115.61±0.04	998.92±0.02	-0.07 ± 0.06	0.35 ± 0.17
33%	5.34 ± 0.10	Al 2p		71.02±0.04	1043.55±0.02	-0.11 ± 0.06	0.62 ± 0.17
		Al 2s		115.83±0.04	998.72±0.02	-0.09 ± 0.06	0.60 ± 0.17
52%	5.85 ± 0.08	Al 2p		70.99±0.04	1043.66±0.02	-0.19 ± 0.06	1.21 ± 0.16
		Al 2s		115.75±0.04	998.90±0.02	-0.19 ± 0.06	1.21 ± 0.16