In-situ MOCVD Growth and Band Offsets of Al₂O₃ Dielectric on β - $Ga_2O_3 \text{ and } \beta$ -(Al_xGa_{1-x})₂O₃ thin films

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Abstract

The in-situ metalorganic chemical vapor deposition (MOCVD) growth of Al₂O₃ dielectrics on β-Ga₂O₃ and β-(Al_xGa_{1-x})₂O₃ films is investigated as a function of crystal orientations and Al compositions of β-(Al_xGa_{1-x})₂O₃ films. The interface and film qualities of Al₂O₃ dielectrics are evaluated by high resolution X-ray diffraction (HR-XRD) and scanning transmission electron microscopy (HR-STEM) imaging, which indicate the growth of high quality amorphous Al₂O₃ dielectrics with abrupt interfaces on (010), (100) and ($\bar{2}01$) oriented β -(Al_xGa_{1-x})₂O₃ films. The surface stoichiometries of Al₂O₃ deposited on all orientations of β-(Al_xGa_{1-x})₂O₃ are found to be well maintained with a bandgap energy of 6.91 eV as evaluated by high resolution x-ray photoelectron spectroscopy, which is consistent with the atomic layer deposited (ALD) Al₂O₃ dielectrics. The evolution of band offsets at both in-situ MOCVD and ex-situ ALD deposited Al₂O₃/β-(Al_xGa_{1-x})₂O₃ are determined as a function of Al composition, indicating the influence of the deposition method, orientation, and Al composition of β-(Al_xGa_{1-x})₂O₃ films on resulting band alignments. Type II band alignments are determined at the MOCVD grown Al₂O₃/β-(Al_xGa_{1-x})₂O₃ interfaces for (010) and (100) orientations, whereas type I band alignments with relatively lower conduction band offsets are observed along ($\overline{201}$) orientation. Results from this study on MOCVD growth and band offsets of amorphous Al₂O₃ deposited on differently oriented β-Ga₂O₃ and β-(Al_xGa_{1-x})₂O₃ films will potentially contribute to design and fabricate future high performance βGa₂O₃ and β-(Al_xGa_{1-x})₂O₃ based transistors using MOCVD in-situ deposited Al₂O₃ as gate dielectric.

Keywords: Ultra-wide bandgap semiconductor, Al_2O_3 dielectric, β - $(Al_xGa_{1-x})_2O_3$ thin film, metalorganic chemical vapor deposition, band offsets

I. Introduction

Beta gallium oxide (β-Ga₂O₃) with its ultrawide bandgap (UWBG) energy (4.5-4.9 eV) and high internal critical breakdown field strength (E_{br, predicted} = 8 MV/cm) has stimulated substantial research interests as an emerging semiconductor material for next generation high power electronics [1]. The controllable n-type doping of β-Ga₂O₃ with excellent transport properties and its availability of differently oriented ((010), (100), ($\bar{2}$ 01) and (001)) single crystal native substrates have paved the way for developing high performance lateral and vertical transistors, Schottky barrier diodes and ultraviolet photodetectors fabricated on high quality β-Ga₂O₃ epi-films [2-19]. Furthermore, alloying β-Ga₂O₃ with Al₂O₃ provides additional band gap engineering over a range of 4.87-8.82 eV [20], and thus a pathway towards enhanced mobility with better device performance based on β-Ga₂O₃/β-(Al_xGa_{1-x})₂O₃ heterostructures [21]. In addition to the successful demonstration of β-Ga₂O₃/β-(Al_xGa_{1-x})₂O₃ based modulation doped field effect transistors (MODFETs) [22-25], the higher predicted breakdown field strength (16 MV/cm for 80% Al content) [26] with controllable n-type doping of β -(Al_xGa_{1-x})₂O₃ [27-29] show a great potential for the development of high-power and high-frequency electronic devices surpassing the state-of-theart.

In recent years, epitaxial development of β -(Al_xGa_{1-x})₂O₃ thin films [30-39] and the implementation of β -(Al_xGa_{1-x})₂O₃/ β -Ga₂O₃ based MODFET devices [22-25] have made

significant progresses. Metalorganic chemical vapor deposition (MOCVD) of β-(Al_xGa_{1-x})₂O₃ thin films on differently oriented β -Ga₂O₃ substrates such as (010) (x \leq 0.35) [28,30,34,35,38], (100) $(x \le 0.52)$ [31,32] and ($\overline{2}01$) $(x \le 0.48)$ [33,38] have been demonstrated. Molecular beam epitaxy (MBE) grown Si delta-doped MODFETs have been demonstrated with decent electron mobility (< 180 cm²/V.s) and relatively high sheet charge density (5 x 10¹² cm⁻²) by using 18-20% Al composition in the β-(Al_xGa_{1-x})₂O₃ layer [22-24]. Recently, a room temperature Hall mobility of 111 cm²/V.s with sheet charge density of 1.06 x 10¹³ cm⁻² was measured in MOCVD grown β-Ga₂O₃/β-(Al_{0.27}Ga_{0.73})₂O₃ modulation-doped heterostructures [25]. To achieve higher density twodimensional electron gases (2DEGs), high Al incorporation in β -(Al_xGa_{1-x})₂O₃ layer with larger β -Ga₂O₃/β-(Al_xGa_{1-x})₂O₃ band offset is required. Apart from the different incorporation efficiency of Al composition in differently oriented β -(Al_xGa_{1-x})₂O₃ thin films [28,31,33], the experimentally measured band offsets at β-Ga₂O₃/β-(Al_xGa_{1-x})₂O₃ heterointerfaces also exhibited a strong dependence on the substrate orientation [38]. The (100) orientated β-Ga₂O₃/β-(Al_xGa_{1-x})₂O₃ heterointerfaces showed relatively higher conduction band offsets as compared to (010) and ($\bar{2}01$) orientations [32,38], indicating potential opportunities for excellent carrier confinement along (100) orientation.

While high quality and high-Al content β -(Al_xGa_{1-x})₂O₃ films with larger β -Ga₂O₃/ β -(Al_xGa_{1-x})₂O₃ band offsets are advantageous for carrier confinement at the heterointerfaces, the quality of the dielectric-semiconductor interface is crucial for reliable high-performance transistors. Several gate dielectric materials such as Al₂O₃, HfO₂, SiO₂ and their alloys or bilayer combinations have been extensively investigated in β -Ga₂O₃ based metal oxide-semiconductor field effect transistors (MOSFETs) [40-45]. While high quality dielectric material with high dielectric constant and lower concentration of interface and bulk traps can significantly improve the performance of β -Ga₂O₃

and β -(Al_xGa_{1-x})₂O₃ based devices, the higher conduction band offset (> 1 eV) at dielectric/ β -Ga₂O₃ (or β-(Al_xGa_{1-x})₂O₃) interfaces is also expected for developing MOS structures with large breakdown field and lower gate leakage. Due to its good compatibility with β-Ga₂O₃, Al₂O₃ with a dielectric constant of 7 - 8.5 has been widely used as a gate dielectric in β-Ga₂O₃ and β-(Al_xGa₁x)2O₃ based devices. Excellent transistor performance in terms of high figure of merits with large breakdown field strength has been demonstrated in (010) and (001) oriented β-Ga₂O₃ based lateral and vertical FET structures using atomic layer deposited (ALD) Al₂O₃ as gate dielectric [15,46,47,48]. However, such ex-situ deposition of Al₂O₃ dielectrics using ALD or sputtering might result in interface contamination due to the exposure of the surface of β-Ga₂O₃ or β-(Al_xGa₁x)2O₃ epi-films to the ambient during loading the samples into different chamber to deposit gate dielectrics. Instead, the in-situ deposition of gate dielectric can potentially avoid such surface or interface contamination of the epi-layer by avoiding the exposure to the ambient atmosphere. Recently, MOCVD in-situ Al₂O₃ deposition on β-Ga₂O₃ is demonstrated with reduced interface traps as compared to the commonly used ALD technique [49], indicating a great potential for depositing high quality gate dielectrics using MOCVD. Moreover, the high temperature deposition of MOCVD (450-1000 °C) with higher deposition rates can improve the quality of the bulk dielectric materials with reduced trap density at the interface. From previous studies, MOCVD in situ growth of amorphous Al₂O₃ on GaN has been demonstrated with lower trap densities (7.4 x 10¹¹ cm⁻²eV⁻¹) and very small hysteresis as compared to the ex-situ ALD Al₂O₃ (1.6 x 10¹² cm⁻² ²eV⁻¹) on GaN MOSCAPs [50]. One of the motivations of this study is to explore the feasibility of in-situ MOCVD growth of amorphous Al₂O₃ on β-Ga₂O₃ and β-(Al_xGa_{1-x})₂O₃, since majority of the dielectric Al₂O₃ on Ga₂O₃ based transistors was deposited by ex-situ ALD. However, further studies are still required to investigate the influence of MOCVD growth conditions on the device

performance while using the in-situ Al₂O₃ as the gate dielectric in transistors. Indeed, MOCVD can provide a wide range of growth conditions that can lead to different interface properties between Al₂O₃ and Ga₂O₃ or (Al_xGa_{1-x})₂O₃. The prior report on ALD deposited Al₂O₃ on (010) β-Ga₂O₃ films revealed the formation of crystalline interlayers of γ-phase Al₂O₃ with 1-5 nm thickness at the interface of Al₂O₃ and β-Ga₂O₃ with lower interface state densities than those of the amorphous Al₂O₃/(-201) β-Ga₂O₃ interface [51], indicating the potential of achieving high quality interfaces due to the crystallization of amorphous Al₂O₃. While MOCVD growth of Al₂O₃ dielectric is demonstrated on both β-Ga₂O₃ [49] and GaN [50, 52] semiconductors, the investigation of the interface quality of in-situ MOCVD deposited Al₂O₃/β-(Al_xGa_{1-x})₂O₃ interfaces are still lacking. Considering the highly orientation dependent band offsets at β- Ga_2O_3/β - $(Al_xGa_{1-x})_2O_3$ interfaces [38], the investigation of the material quality of Al_2O_3 dielectric deposited on differently oriented β-(Al_xGa_{1-x})₂O₃ interfaces with different Al compositions are still in need. Moreover, the accurate extraction of the band offsets at dielectric/β-(Al_xGa_{1-x})₂O₃ interface is also critical for designing and fabricating β-(Al_xGa_{1-x})₂O₃ based devices. Nevertheless, information related to the band discontinuities at the interface of Al₂O₃ dielectric and differently oriented β -(Al_xGa_{1-x})₂O₃ as a function of Al composition are not reported yet.

In this work, we have systematically investigated the interface quality of in-situ MOCVD grown Al₂O₃ dielectric on (010), (100) and ($\bar{2}01$) oriented β -Ga₂O₃ and β -(Al_xGa_{1-x})₂O₃ thin films and experimentally determined the band offsets at Al₂O₃(dielectric)/ β -(Al_xGa_{1-x})₂O₃ heterointerfaces with various Al compositions along different orientations. Moreover, the band offsets determined for MOCVD in-situ Al₂O₃ are also compared with ALD (ex-situ) Al₂O₃ deposited on β -(Al_xGa_{1-x})₂O₃ interfaces.

II. Experimental Section

The β -(Al_xGa_{1-x})₂O₃ thin films were grown on Fe doped semi-insulating (010), (100), and (201) oriented β-Ga₂O₃ substrates (purchased from Novel Crystal Technology, Inc), with an unintentionally doped (UID) ~ 65 nm thick β-Ga₂O₃ as buffer layer via Agnitron Technology Agilis R&D MOCVD system. Triethylgallium (TEGa), Trimethylaluminum (TMAl), and pure O₂ were used as Ga, Al, and O precursors, respectively. Argon (Ar) was used as the carrier gas. The different Al compositions (x = 0 - 52%) of differently oriented β -(Al_xGa_{1-x})₂O₃ films were obtained by systematically tuning the [TMAI]/[TMAI+TEGa] molar flow ratio, growth temperature (880 °C), chamber pressure (20-80 torr) and group VI/III ratio [28,30,31,33]. To minimize potential contaminations from the growth surface, all substrates were cleaned ex-situ by using solvents and then in-situ by high temperature (920°C) annealing for 5 mins under O₂ atmosphere before the growths start. On top of the β-(Al_xGa_{1-x})₂O₃ thin films, a 40 nm thick Al₂O₃ dielectric layer was deposited in the same MOCVD chamber at a growth temperature of 700 °C and chamber pressure of 20 torr. The O₂ flow rate was fixed at 500 sccm. The Al₂O₃ deposition rate of 4 nm/min was obtained with TMAl molar flow rate of 5.46 µmol/min. For the band offset measurements by using XPS, three types of samples were prepared as shown in Figure S1 of the supplementary material: (a) 20-60 nm thick β -(Al_xGa_{1-x})₂O₃ films grown on UID β -Ga₂O₃ buffer layer on top of (010), (100) and ($\bar{2}01$) β -Ga₂O₃ substrates, (b) ~ 40 nm thick, and (c) thin (~2-5 nm) Al₂O₃ deposited on (010), (100) and ($\bar{2}01$) oriented β -(Al_xGa_{1-x})₂O₃ films with different Al compositions. The ALD deposition of Al₂O₃ was performed in a Picosun SUNALE R-150B by using Trimethylaluminum (TMAI) as the Al precursor and water (H₂O) as the O₂ precursor. For the band offset measurements, on top of the MOCVD grown differently oriented β-(Al_xGa_{1-x})₂O₃ films, Al₂O₃ layers with thick (~50 nm) and thin (~3 nm) thicknesses were deposited at 300 °C in the ALD

chamber. Prior to the loading into the ALD chamber, all β -(Al_xGa_{1-x})₂O₃ samples were cleaned using acetone, IPA, and DI water.

High resolution XRD using a Bruker D8 Discover was performed to evaluate the quality and structures of Al₂O₃ dielectrics and β -(Al_xGa_{1-x})₂O₃ epi-films oriented along different directions. Surface morphologies were evaluated by atomic force microscopy (AFM) using Bruker AXS Dimension Icon. Surface stoichiometry, band gap energies and band offsets at Al₂O₃/β-(Al_xGa₁-_x)₂O₃ were determined using XPS measurements with an energy resolution of 0.1 eV. A Kratos Axis Ultra X-ray photoelectron spectrometer using monochromic Al Kα x-ray source with a photon energy of 1486.6 eV was used for the XPS measurement. C 1s peak (284.8 eV) from the adventitious carbon was used as a reference to calibrate the binding energy. As the bandgaps and band offsets at Al₂O₃/β-(Al_xGa_{1-x})₂O₃ were determined using the binding energy differences between the core level peak positions of any given sample, the correction of the peak positions does not impact the results. The electron pass energy was set at 20 eV during high resolution scanning and 80 eV for survey scanning. A Thermo Fisher Scientific Themis-Z scanning transmission electron microscope (200 kV, Cs3=0.002 mm, and Cs5=1.0 mm) with probe convergence half angles of 17.9 mrad was utilized to perform high resolution STEM high angle annular dark filed (HAADF) imaging.

III. Results and Discussions

To evaluate the crystalline phase and quality of the in-situ MOCVD deposited Al_2O_3 dielectrics grown on differently oriented β -Ga₂O₃ thin films, high resolution XRD was performed. Figures 1 (a)-(c) show the XRD ω -2 θ scans of the \sim 40 nm thick Al_2O_3 dielectrics deposited on top of 65 nm thick UID β -Ga₂O₃ buffer layer on (100), ($\bar{2}01$) and (010) oriented β -Ga₂O₃ substrates,

respectively. The Al₂O₃ dielectrics were deposited at a growth temperature of 700 °C. While high intensity distinguishable peaks originated from differently oriented β-Ga₂O₃ substrates are observed for all orientations, no other well-resolved XRD peaks corresponding to different crystalline phases/orientations of Al₂O₃ films are visible in wide range scans, indicating that the MOCVD deposited Al₂O₃ films possess amorphous structures for all different orientations of substrates, which is also evidenced from STEM imaging as discussed in the later sections. Our previous studies demonstrated the growth of γ-phase Al₂O₃ thin films on (010) β-Ga₂O₃ substrate at relatively higher growth temperature (880 °C) [30], suggesting that the lower growth temperature (700 °C) is a key parameter that can lead to the deposition of amorphous Al₂O₃ dielectrics on β-Ga₂O₃. The surface RMS roughness of a gate dielectric is also a critical parameter that has a significant impact on device performance. Figures 2 (a)-(c) show the surface RMS roughness of ~ 40 nm thick Al₂O₃ dielectric deposited in MOCVD chamber on (010), (100) and (201) β-Ga₂O₃ films, respectively. Smooth and uniform surface morphologies of Al₂O₃ with RMS roughness of 1.42 nm (010), 1.25 nm (100), and 1.17 nm ($\bar{2}01$) are observed on differently oriented β-Ga₂O₃ films. The lowest surface morphologies observed on ($\bar{2}01$) β-Ga₂O₃ films as compared to those of (010) and (100) \(\beta\)-Ga₂O₃, indicating a strong dependence of the surface morphologies of top Al₂O₃ dielectrics on the orientations of β -Ga₂O₃ substrates.

The quality of Al_2O_3 dielectrics and the interfacial abruptness of MOCVD deposited Al_2O_3/β - Ga_2O_3 (β - $(Al_xGa_{1-x})_2O_3$) for different orientations are investigated using high-resolution STEM imaging and energy dispersive x-ray spectroscopy (STEM-EDS) elemental mapping. High resolution HAADF STEM images for $Al_2O_3/(010)$ β - Ga_2O_3 and $Al_2O_3/(010)$ β - $(Al_{0.17}Ga_{0.83})_2O_3$ are shown in Figures 3 (a) and (b), respectively. The high resolution HAADF-STEM images of Al_2O_3 dielectric deposited on $(\overline{2}01)$ and (100) oriented β - Ga_2O_3 and β - $(Al_{0.17}Ga_{0.83})_2O_3$ thin films

are also shown in Figures 3 (c) and (d) [($\overline{2}01$) orientation] and (e) and (f) [(100) orientation], respectively. The growth of amorphous Al₂O₃ dielectrics on top of β -Ga₂O₃ and β -(Al_{0.17}Ga_{0.83})₂O₃ layers is confirmed from the atomic resolution STEM images. The sharp contrasts between Al₂O₃ dielectric (dark) and β -Ga₂O₃ (β -(Al_{0.17}Ga_{0.83})₂O₃) (bright) indicate high quality interfaces along all investigated orientations.

STEM-EDS spectroscopy also reveals abrupt and sharp interfaces between Al₂O₃ and (010) oriented β-Ga₂O₃ and β-(Al_{0.17}Ga_{0.83})₂O₃ as shown in Figures 4 (a-h) and Figures S2 and S3 of the supplementary materials. The EDS color maps of Ga (green) and Al (blue) elements in Figures 4 (a-d) $[Al_2O_3/\beta-Ga_2O_3]$ and (e-h) $[Al_2O_3/\beta-(Al_{0.17}Ga_{0.83})_2O_3]$ and elemental mapping (Figs. 4 (d) and (h)) also confirm the interfacial abruptness between Al₂O₃ and (010) oriented β-Ga₂O₃ (β- $(Al_{0.17}Ga_{0.83})_2O_3$). Figures 5 (a-d) and (e-h) show the HAADF-STEM images of $Al_2O_3/(\overline{2}01)$ β - Ga_2O_3 (Fig. 5(a)) and $Al_2O_3/(\bar{2}01)$ β -($Al_{0.17}Ga_{0.83}$)₂O₃ (Fig. 5(e)) interfaces with corresponding EDS maps of (b, f) Al, (c, g) Ga and (d, h) O elements. The abrupt transition of Ga and Al at $Al_2O_3/(\overline{2}01)$ β -Ga₂O₃ (β -(Al_{0.17}Ga_{0.83})₂O₃) interfaces are observed for both samples, as also shown in Figures S4 and S5 of the supplementary materials, with a very slight interdiffusion of Ga and Al atoms at the interfaces. The abruptness of the interfaces between Al₂O₃ and (100) oriented β- Ga_2O_3 (β -(Al_xGa_{1-x})₂ O_3) is also evaluated by cross-sectional HAADF-STEM images and EDS elemental mapping of Al₂O₃/β-Ga₂O₃ and Al₂O₃/β-(Al_{0.17}Ga_{0.83})₂O₃ as shown in Figures 6 (a-d) and (e-h), (Figs. S6 and S7 of the supplementary materials) respectively. The EDS color maps of Al (blue) and Ga (green) components in Figures 6 (b, c) and (f, g) correspond to the Ga and Al concentrations of the samples as indicated by the EDS quantitative line scan (Figs. 6(d, h)) along the orange arrows in Figures 6 (a, e) reveal sharp and high-quality interfaces between Al₂O₃ dielectric and (100) oriented β -Ga₂O₃ (β -(Al_{0.17}Ga_{0.83})₂O₃) layers.

The surface stoichiometry of in-situ MOCVD deposited Al₂O₃ dielectric are investigated by using high resolution XPS. The O 1s, Al 2s and 2p core level data were used to determine the O and Al percentage in Al₂O₃ dielectric. Figures 7 (a-c) show the O 1s, Al 2s and Al 2p spectra for a representative Al₂O₃ film deposited on (010) β -Ga₂O₃. The peaks are fitted with Gaussian-Lorentzian function after subtracting by Shirley type background. The O 1s peak is fitted with two components, O-Al bond at 531.1 eV and O-H bond at 532.1 eV, as shown in Figure 7(a). The Al 2s and Al 2p core level peaks are fitted with single peak as shown in Figures 7(b) and (c), respectively. Using the relative sensitivity factors of O 1s, Al 2s and Al 2p peaks (S_{O 1s} = 2.93, S_{Al 2s} = 0.753 and S_{Al 2p} = 0.5371), the percentage of Al and O in Al₂O₃ dielectric is determined to be 40.39% and 59.61%, respectively. The list of all Al and O percentages in both MOCVD and ALD deposited Al₂O₃ on other orientations ((($\overline{2}$ 01)) and (100)) of β -Ga₂O₃ are included in Table S1 of the supplementary materials, indicating that the surface stoichiometries of Al₂O₃ deposited by using both MOCVD and ALD methods are well maintained on all investigated orientations.

By utilizing XPS, the bandgap of MOCVD deposited Al_2O_3 is estimated by measuring the onset of inelastic loss spectrum of O 1s core level peak. The estimation of the bandgap energies of wide bandgap semiconductor materials using the inelastic loss curve appeared on higher binding energy side of a high intensity XPS core level spectra is a well-established method [53-61]. The lower limit of inelastic scattering represents the bandgap of a material as the lowest energetically inelastic scattering that an electron experiences during its travelling from the bulk to the surface is the excitation from the valence band to the conduction band. Figure 8(a) shows the O 1s core level peak for a representative Al_2O_3 sample grown on (010) oriented β -Ga₂O₃ film. The onset is determined from the intersection of the linear extrapolation of the loss spectra curve and constant background as shown in Figure 8(b). The bandgap of MOCVD deposited Al_2O_3 is estimated as

6.91 eV from the separation between the onset and O 1s peak positions. Similarly, the ALD deposited Al₂O₃ also exhibited a bandgap energy of 6.88 eV, which is well consistent with the bandgap energy reported previously from different deposition methods [55-57, 62-64]. The bandgap determined by Reflection Electron Energy Loss Spectroscopy were estimated as 6.9 eV for Al₂O₃ deposited by either ALD or sputtering method [62-64], which are found to be very consistent with our extracted bandgap values by using XPS. Apart from these studies, the band gap of amorphous Al₂O₃ was determined to be 7.0 ± 0.1 eV by using Al 2p and O 1s photoelectron spectra [55]. In addition, 6.8 eV of bandgap energy were measured using O 1s core-level binding energy spectrum of ALD-Al₂O₃ on (010) Ga₂O₃ [56]. Similarly, from the energy separation between the main O 1s line and the loss threshold, a bandgap of 7.0 ± 0.1 eV was determined for the 120 nm thick Al₂O₃ film deposited on 6H-SiC [57]. These studies indicate that our measured bandgap of both MOCVD and ALD deposited Al₂O₃ are in a good agreement with previous reports. Using the same approach, the extraction of bandgap energies of (010), (100) and ($\overline{2}01$) oriented β -Ga₂O₃ and β -(Al_xGa_{1-x})₂O₃ with different Al compositions [38] are listed in Table S2 of the supplementary material.

The band offsets at the interfaces of Al_2O_3 with all three orientations ((010), (100) and ($\bar{2}01$)) of β -Ga₂O₃ and β -(Al_xGa_{1-x})₂O₃ for a wide Al composition range are determined by using XPS. The valence band offsets (ΔE_v) at Al_2O_3/β -Ga₂O₃ (β -(Al_xGa_{1-x})₂O₃) are determined by using the Kraut's method [65]. Using the bandgaps of Al_2O_3 , β -Ga₂O₃ and β -(Al_xGa_{1-x})₂O₃ and ΔE_v values, the corresponding conduction band offsets (ΔE_c) are estimated as follows:

$$\Delta E_{v} = (E_{Ga\,3s}^{AlGaO} - E_{VBM}^{AlGaO}) - (E_{Al\,2p}^{AlO} - E_{VBM}^{AlO}) - (E_{Ga\,3s}^{AlGaO/AlO} - E_{Al\,2p}^{AlGaO/AlO})$$
(1)

$$\Delta E_c = E_g^{AlO} - E_g^{AlGaO} - \Delta E_v$$
 (2)

where $E_{Ga\ 3s}^{AlGaO/AlO}$ are the binding energies of Ga 3s core levels in β -(Al_xGa_{1-x})₂O₃ bulk material and Al_2O_3/β -(Al_xGa_{1-x})₂O₃ interfaces, respectively. $E_{Al\ 2p}^{AlO}$ and $E_{Al\ 2p}^{AlGaO/AlO}$ are the Al 2p core level binding energies of Al_2O_3 bulk material and Al_2O_3/β -($Al_xGa_{1.x}$)₂O₃ interfaces, respectively. E_{VBM}^{AlGaO} and E_{VBM}^{AlO} are the valence band maxima (VBM) positions of β -(Al_xGa_{1-x})₂O₃ and Al_2O_3 bulk materials, respectively. E_g^{AlO} and E_g^{AlGaO} are the bandgap energies of the Al_2O_3 and β -(Al_xGa_{1-x})₂O₃ thin films, respectively.

The fitted Ga 3s, Al 2p core level peaks and the valence band (VB) spectra are shown in Figures 9(a)-(f) for the in-situ MOCVD deposited Al₂O₃ on (010) oriented β-(Al_{0.17}Ga_{0.83})₂O₃ thin films. The Ga 3s (Figs. 9(a) and (e)) and Al 2p (Figs. 9(c) and (f)) core level peak positions for bulk β -(Al_{0.17}Ga_{0.83})₂O₃ (Figs. 9(a)), Al₂O₃ (Figs. 9(c)) and Al₂O₃/ β -(Al_{0.17}Ga_{0.83})₂O₃ heterostructure (Figs. 9(e) and (f)) are determined by fitting with mixed Lorentzian-Gaussian line shapes after applying the Shirley type background subtraction. Both Ga 3s and Al 2p core levels are fitted with the single peak. The VBM positions from bulk β-($Al_{0.17}Ga_{0.83}$)₂O₃ (Figs. 9(b)) and Al₂O₃ (Figs. 9(d)) are determined by the linear extrapolation of the leading edge of the VB spectra to the background. The ΔE_v of -0.18 eV is determined at the $Al_2O_3/(010)$ β - $(Al_{0.17}Ga_{0.83})_2O_3$ interface by using equation (1). By using the ΔE_v value and bandgaps of Al₂O₃ and (010) β - $(Al_{0.17}Ga_{0.83})_2O_3$, the ΔE_c of 2.06 eV is determined from equation (2). Using similar approach, the band offsets at the interfaces between MOCVD (and ALD) deposited Al₂O₃ dielectrics and differently oriented β-Ga₂O₃ and β-(Al_xGa_{1-x})₂O₃ heterostructures for all investigated Al compositions are determined. The band offsets determined by using Ga 3s and Al 2p core levels are also verified by comparing with those extracted from Ga 3s/Ga 3d and Al 2p / Al 2s core levels as listed exemplarily for Al₂O₃/(010) β-(Al_xGa_{1-x})₂O₃ interfaces in Table 1 and Tables S2 and S3 of the supplementary material for other Al_2O_3/β - $(Al_xGa_{1-x})_2O_3$ interfaces along different orientations and deposition methods, indicating a good consistency between the band offsets values estimated from different core level spectra.

Heterostructures are classified as Type I and Type II depending on the alignment of the bands producing the discontinuity. While one material's band gap overlaps another's in Type I- straddling heterostructures, both conduction and valence band edges of a material are lower than the corresponding band edges of another material in Type II- staggered heterostructure. The band alignment diagram of MOCVD deposited Al₂O₃/β-Ga₂O₃ (β-(Al_xGa_{1-x})₂O₃) heterostructures are shown in Figures 10 (a)-(c) for (010), (100) and ($\bar{2}01$) orientations, respectively. Type II (staggered) band alignment at the interfaces of Al₂O₃ deposited on (010) and (100) oriented β-(Al_xGa_{1-x})₂O₃ is determined for all investigated Al compositions, whereas the $(\bar{2}01)$ orientations show type I (straddling) band alignment between Al_2O_3 and β -(Al_xGa_{1-x})₂ O_3 . The valence band offsets are found to vary from -0.07 to -0.17 eV (010), -0.14 to -0.23 eV (100) and 0.20 to 0.27 eV ($\overline{2}01$) with corresponding conduction band offsets ranging between 2.14 and 1.66 eV (010), 2.22 and 1.29 eV (100), and 1.79 to 0.9 eV ($\bar{2}01$) as the Al compositions in differently oriented β -(Al_xGa_{1-x})₂O₃ are varied from 0 to 35% (010), 0 to 52% (100) and 0 to 48% ($\bar{2}01$). Similarly, the evolution of the band alignments at the interfaces of ALD deposited Al₂O₃ with the MOCVD grown β-(Al_xGa₁- $_{\rm x}$)₂O₃ with different Al compositions are shown in Figures 11 (a)-(c) for (010), (100) and ($\bar{2}$ 01) orientations, respectively. As the Al composition varies, the valence and conduction band offsets range from -0.12 to -0.35 eV (ΔE_v) and 2.18 to 1.81 eV (ΔE_c) (for (010) orientation), -0.31 to -0.55 eV (ΔE_v) and 2.36 to 1.44 eV (ΔE_c) (for (100) orientation) and 0.07 to 0.29 eV (ΔE_v) and 1.74 eVto 0.89 eV (ΔE_c) (for ($\bar{2}01$) orientation), respectively. Similar to the in-situ MOCVD deposited Al₂O₃, type II band alignments are observed for both (010) and (100) orientations and type I band

discontinuity is observed at the interface of ALD Al₂O₃/($\overline{2}01$) β -(Al_xGa_{1-x})₂O₃. For both MOCVD and ALD deposition of Al₂O₃, the conduction band offsets exhibit relatively larger variations with Al compositions as compared to the valence band offsets for all three orientations. Such lower ΔE_v (0.25 eV) as compared to the conduction band offset (ΔE_c) of 2.06 eV was also demonstrated between the interface of amorphous Al₂O₃ and monoclinic β -Ga₂O₃ [66] by using the band-edge position information of amorphous Al₂O₃ from experimentally determined band gap and valence-band offset with corundum α -phase Al₂O₃ [55].

The evolution of the valence and conduction band offsets of both in-situ MOCVD and ALD grown Al₂O₃ dielectrics on β-(Al_xGa_{1-x})₂O₃ heterointerfaces are represented in Figures 12 (a)-(d) as a function of Al composition for different orientations. The general trend shows that both ΔE_v and ΔE_c values decrease as the Al compositions in β -(Al_xGa_{1-x})₂O₃ increases, with a much weaker variation in the ΔE_v values as compared to the corresponding changes in ΔE_c values. Although both deposition methods showed type II band discontinuity along (010) and (100) orientations and type I band alignment along ($\bar{2}01$) orientations, the variations in the values of ΔE_v and ΔE_c between MOCVD and ALD deposited Al₂O₃/β-(Al_xGa_{1-x})₂O₃ heterointerfaces can be attributed to the quality of the bulk Al₂O₃ and Al₂O₃/β-(Al_xGa_{1-x})₂O₃ interfaces as the deposition of Al₂O₃ is performed under completely different growth environments. Previously, type I straddling gap band alignment was demonstrated on ALD Al₂O₃ on $(\bar{2}01)$ β -Ga₂O₃, whereas sputtered Al₂O₃ showed a type II staggered gap with β-Ga₂O₃ [62]. Similar changes of band alignment from type I to type II are also observed as the Al₂O₃ deposition methods changed from ALD to sputtering on $(010) \beta$ - $(Al_{0.14}Ga_{0.86})_2O_3$ interfaces [64], revealing a strong influence of the synthesis method on the resulting band alignment. In this work, for both MOCVD and ALD deposition, the Al₂O₃/ $(\overline{2}01)$ β -(Al_xGa_{1-x})₂O₃ interfaces show the smallest conduction band offsets

as compared to the (010) and (100) orientations, with a type I band alignment (Figs. 12(b,d)). While a small variation in ΔE_v (Fig. 12(a)) and ΔE_c (Fig. 12(b)) values between the (010) and (100) orientations are observed for in-situ MOCVD deposited Al₂O₃/ β -(Al_xGa_{1-x})₂O₃ interfaces, the ALD deposited Al₂O₃ on (100) oriented β -(Al_xGa_{1-x})₂O₃ exhibits relatively higher ΔE_v (Fig. 12(c)) and ΔE_c (Fig. 12(d)) values as compared to other orientations, indicating a strong dependence of the band offsets on dielectric deposition methods, crystalline orientations and Al compositions of β -(Al_xGa_{1-x})₂O₃ films.

IV. Conclusion

In summary, in-situ MOCVD growth of Al₂O₃ dielectrics with high quality Al₂O₃/β-(Al_xGa₁x)2O₃ interfaces are successfully demonstrated on different orientations of β-(Al_xGa_{1-x})2O₃ as a function of Al composition. The growth of high quality amorphous Al₂O₃ dielectrics with sharp interfaces and good surface stoichiometry are revealed by comprehensive characterization of high resolution XRD, STEM and XPS. As compared to (010) and (100) orientations, relatively lower RMS roughness is observed for Al₂O₃ dielectrics deposited on (201) β-Ga₂O₃, indicating an influence of crystal orientation of underlying β-Ga₂O₃ on the surface morphologies of top Al₂O₃ dielectric. The band offsets between in-situ MOCVD and ALD deposited Al₂O₃ dielectric and β-(Al_xGa_{1-x})₂O₃ interfaces are investigated systematically for a wide range of Al compositions, revealed a strong influence of deposition methods, orientations, and Al composition of β-(Al_xGa₁x)2O₃ films on the valence and conduction band offsets. A type-II band alignment at Al₂O₃/β-(Al_xGa_{1-x})₂O₃ interfaces for all investigated Al compositions are observed for (010) and (100) oriented β -(Al_xGa_{1-x})₂O₃ films, whereas type-I band alignment is observed for ($\overline{2}01$) orientation with relatively lower ΔE_c values for both deposition methods. A weaker variation in ΔE_v values with different Al compositions of β -(Al_xGa_{1-x})₂O₃ are observed as compared to the variation in ΔE_c values. The high quality MOCVD growth of Al_2O_3 on differently oriented β -Ga₂O₃ and β -(Al_xGa_{1-x})₂O₃ films with sharp interfaces and the information on orientation dependent band offsets will be useful for the understanding, modeling and fabrication of β -Ga₂O₃ and β -(Al_xGa_{1-x})₂O₃ based MOS devices.

See the supplementary material for the schematic of the samples grown for band offset measurements, summary of the O and Al percentage of Al₂O₃ dielectrics calculated by using O 1s and Al 2p/Al 2s core level XPS spectra, and the summary of the band offsets at MOCVD in-situ and ALD ex-situ deposited Al₂O₃/β-(Al_xGa_{1-x})₂O₃ interfaces.

Conflict of Interest Statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Supplementary Material

See supplementary material for XPS data for determining the band offsets and STEM-EDS maps.

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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 Caption

Table 1. Summary of the valence and conduction band offsets at $Al_2O_3/(010)$ β - $(Al_xGa_{1-x})_2O_3$ interfaces, determined by using the VBM, Ga 3s, Ga 3d and Al 2p core level peak positions.

Figure Captions

Figure 1. XRD ω -2 θ scans of in-situ MOCVD grown \sim 40 nm thick Al₂O₃ dielectrics on (a) (010), (b) ($\bar{2}$ 01), and (c) (100) β -Ga₂O₃ substrates.

Figure 2. Surface AFM images (scan area: $5x5 \mu m^2$) of MOCVD deposited Al₂O₃ dielectrics on (a) (010), (b) ($\bar{2}01$), and (c) (100) β-Ga₂O₃ substrates.

Figure 3. High resolution HAADF-STEM cross-sectional images of in-situ MOCVD deposited Al_2O_3 dielectrics grown on (a) (010) β- Ga_2O_3 , (b) (010) β- $(Al_{0.17}Ga_{0.83})_2O_3$, (c) ($\overline{2}01$) β- Ga_2O_3 , (d) ($\overline{2}01$) β- $(Al_{0.17}Ga_{0.83})_2O_3$, (e) (100) β- Ga_2O_3 , and (f) (100) β- $(Al_{0.17}Ga_{0.83})_2O_3$ layers. The HAADF-STEM images for $Al_2O_3/(\overline{2}01)$ β- Ga_2O_3 (β- $(Al_{0.17}Ga_{0.83})_2O_3$) are taken from [001] zone axis and $Al_2O_3/(\overline{2}01)$ and (100) oriented β- Ga_2O_3 (β- $(Al_{0.17}Ga_{0.83})_2O_3$) are taken from [010] zone axis.

Figure 4. STEM-EDS maps for MOCVD deposited Al₂O₃ dielectrics on (a-d) (010) β-Ga₂O₃ and (e-h) (010) β-(Al_{0.17}Ga_{0.83})₂O₃. HAADF images of (a) Al₂O₃/(010) β-Ga₂O₃ and Al₂O₃/(010) β-(Al_{0.17}Ga_{0.83})₂O₃ with corresponding (b,f) Al and (c,g) Ga EDS maps and (d,h) atomic fraction elemental profiles as indicated by the orange arrow in (a, e).

Figure 5. STEM-EDS for maps MOCVD Al₂O₃ dielectrics deposited on (a-d) ($\bar{2}01$) β-Ga₂O₃ and (e-h) ($\bar{2}01$) β-(Al_{0.17}Ga_{0.83})₂O₃. HAADF images of (a) Al₂O₃/($\bar{2}01$) β-Ga₂O₃ and Al₂O₃/($\bar{2}01$) β-(Al_{0.17}Ga_{0.83})₂O₃ with corresponding (b,f) Al and (c,g) Ga EDS maps and (d,h) atomic fraction elemental profiles as indicated by the orange arrow in (a, e).

Figure 6. STEM-EDS maps for MOCVD Al₂O₃ dielectrics deposited on (a-d) (100) β-Ga₂O₃ and (e-h) (100) β-(Al_{0.17}Ga_{0.83})₂O₃. HAADF images of (a) Al₂O₃/(100) β-Ga₂O₃ and Al₂O₃/(100) β-Ga₂O₃/(100) β-Ga₂O₃/(100) β-Ga₂O₃/(100) β-Ga₂O₃/(100) β-Ga

(Al_{0.17}Ga_{0.83})₂O₃ with corresponding (b,f) Al and (c,g) Ga EDS maps and (d,h) atomic fraction elemental profiles as indicated by the orange arrow in (a, e).

Figure 7. XPS (a) O 1s, (b) Al 2s and (c) Al 2p core level spectra for in-situ MOCVD grown Al₂O₃ dielectrics on (010) β-Ga₂O₃ substrates. Experimental data points (black open circles) are fitted using mixed Lorentzian-Gaussian line shapes (black solid lines) after applying the Shirley background (gray solid lines) subtraction.

Figure 8. (a) The bandgap energy estimated by using the onset of inelastic loss spectra of O 1s core level peak from in-situ MOCVD grown Al₂O₃ dielectrics on (010) β-(Al_{0.17}Ga_{0.83})₂O₃. (b) zoomed view of the background region of the O 1s core level.

Figure 9. Fitted (a) Ga 3s and (b) valence band (VB) spectra from (010) β-(Al_{0.17}Ga_{0.83})₂O₃ and (c) Al 2p and (d) VB spectra from ~40 nm thick Al₂O₃ deposited in-situ by MOCVD. The fitted Ga 3s and Al 2p core levels from Al₂O₃/(010) β-(Al_{0.17}Ga_{0.83})₂O₃ heterointerfaces are shown in (e) and (f), respectively. Experimental data are shown as black open circles and the fitted curves (envelope) are represented as black sloid lines.

Figure 10. The band alignments at the interfaces of in-situ MOCVD deposited Al_2O_3 and (a) (010) β-(Al_xGa_{1-x})₂ O_3 (x = 0 - 0.35) (b) (100) β-(Al_xGa_{1-x})₂ O_3 (x = 0 - 0.52) and (c) ($\overline{2}$ 01) oriented β-(Al_xGa_{1-x})₂ O_3 (x = 0 - 0.48).

Figure 11. The band alignments at the interfaces of ALD deposited Al₂O₃ and (a) (010) β-(Al_xGa_{1-x})₂O₃ (x = 0 - 0.35) (b) (100) β-(Al_xGa_{1-x})₂O₃ (x = 0 - 0.52) and (c) ($\overline{2}01$) oriented β-(Al_xGa_{1-x})₂O₃ (x = 0 - 0.48).

Figure 12. The evolution of the (a,c) valence band offsets (considering the valence band maxima position of Al₂O₃ at 0 eV) and (b,d) conduction band offsets at the interfaces of (a,b) in-situ

MOCVD and (c,d) ALD deposited Al_2O_3 and differently oriented β -(Al_xGa_{1-x}) $_2O_3$ as a function of Al compositions.

Table 1.

Ga 3s and Al 2p:

Sample	E _g (± 0.20 eV)	EAlGaO- Ga 3s - EAlGaO (± 0.04 eV)	$\begin{array}{c} E_{Al2p}^{Al0} - \\ E_{VBM}^{Al0} \\ (\pm~0.04 \\ eV) \end{array}$	$E_{G\alpha3s}^{\text{AlGaO/AlO}}-E_{\text{Al GaO/AlO}}^{\text{AlGaO/AlO}}-E_{\text{Al 2p}}^{\text{AlGaO/AlO}}$ $(\pm0.02\;\text{eV})$	ΔE _v (eV) (± 0.06 eV)	ΔE _c (eV) (± 0.29 eV)
Al_2O_3	6.91		71.23			
β-Ga ₂ O ₃	4.84	157.43		86.27	-0.07	2.14
β -(Al _{0.17} Ga _{0.83}) ₂ O ₃	5.03	157.38		86.32	-0.18	2.06
β -(Al _{0.35} Ga _{0.65}) ₂ O ₃	5.42	157.47		86.40	-0.17	1.66

Ga 3d and Al 2p:

Sample	E _g (± 0.20 eV)	$\begin{array}{c} E_{Ga}^{AlGaO} - \\ E_{Ga}^{AlGaO} - \\ E_{VBM}^{VBM} \\ (\pm 0.04 \\ eV) \end{array}$	$E_{Al2p}^{Al0}-\\E_{VBM}^{Al0}\\(\pm0.04\\eV)$	$E_{Ga\;3d}^{\text{AlGaO/AlO}}-E_{\text{Al}\;\text{GaO/AlO}}^{\text{AlGaO/AlO}}$ $(\pm\;0.02\;\text{eV})$	$\begin{array}{c} \Delta E_v \\ (eV) \\ (\pm 0.06 \\ eV) \end{array}$	ΔE _c (eV) (± 0.29 eV)
Al ₂ O ₃	6.91		71.23			
β-Ga ₂ O ₃	4.84	16.87		-54.32	-0.05	2.12
β -(Al _{0.17} Ga _{0.83}) ₂ O ₃	5.03	16.79		-54.30	-0.14	2.02
β -(Al _{0.35} Ga _{0.65}) ₂ O ₃	5.42	16.87		-54.24	-0.12	1.61

Figure 1.

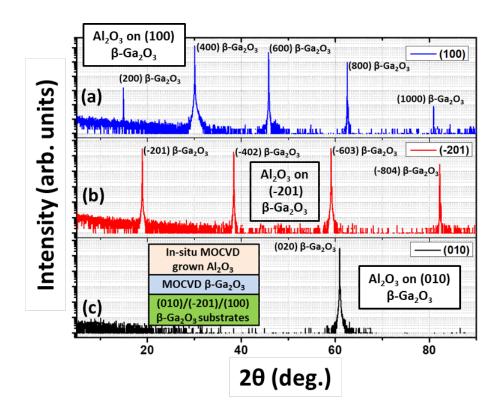


Figure 2.

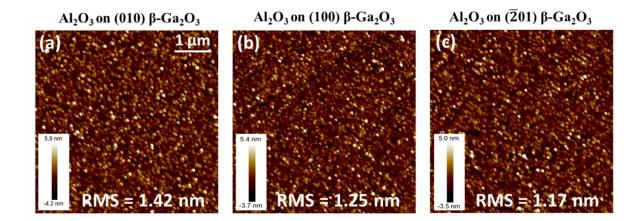


Figure 3.

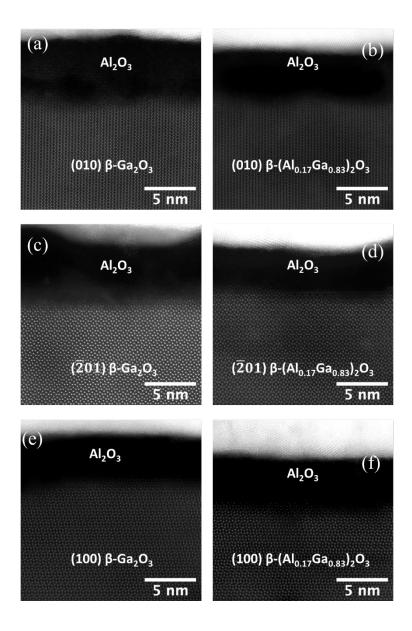


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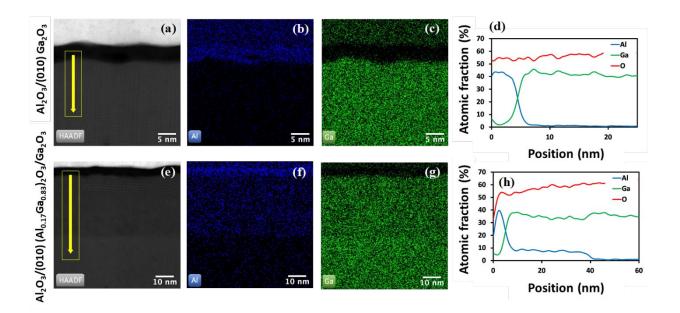


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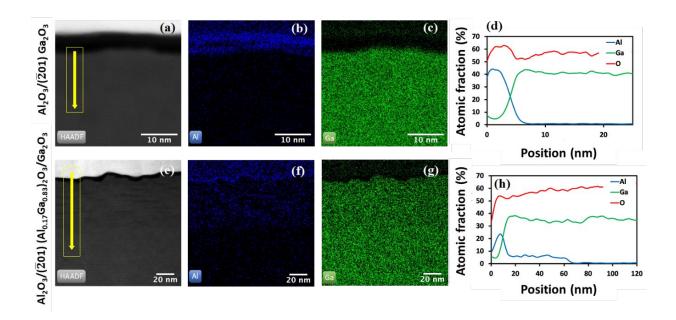


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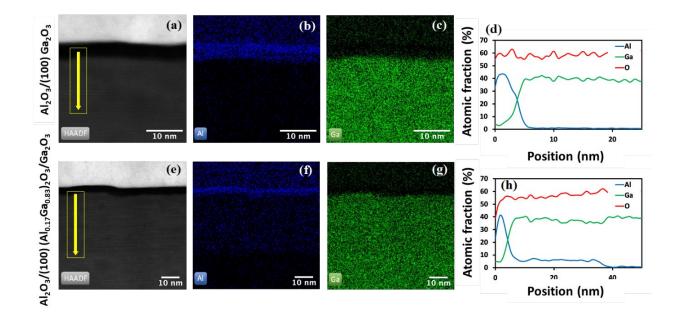


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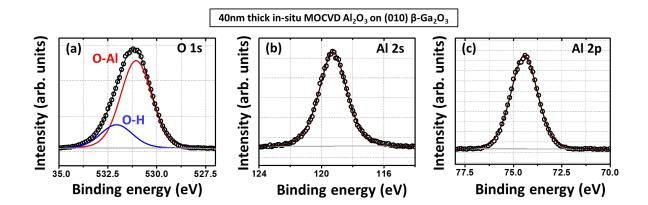


Figure 8.

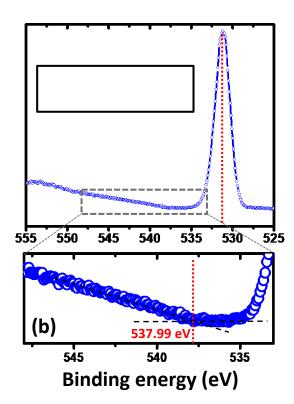


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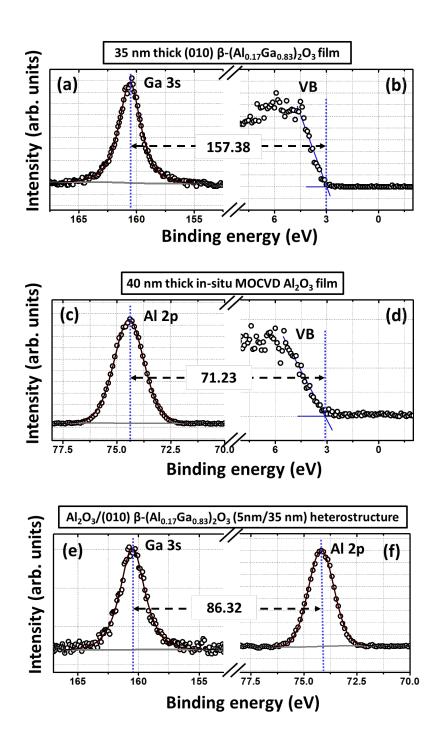
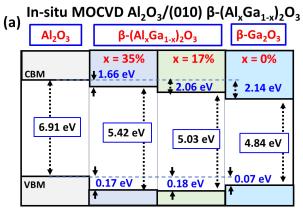
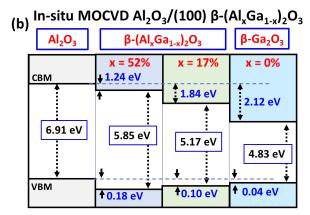


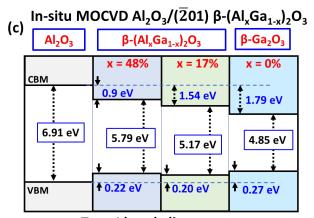
Figure 10.



Type II band alignment

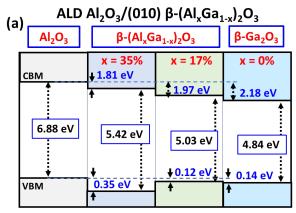


Type II band alignment

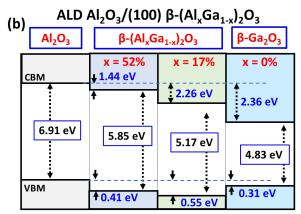


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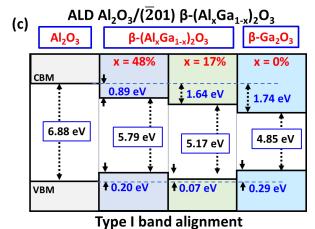
Figure 11.



Type II band alignment



Type II band alignment



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Figure 12.

