Energy-band parameters of atomic layer deposited Al\textsubscript{2}O\textsubscript{3} and HfO\textsubscript{2} on In\textsubscript{x}Ga\textsubscript{1−x}As

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X-ray photoelectron spectroscopy (XPS) combined with reflection electron energy loss spectroscopy (REELS) were used to determine the energy-band parameters, valence-band offsets \(\Delta E_{v}\), conduction-band offsets \(\Delta E_{c}\), and energy-band gaps \(E_{g}\) of the atomic layer deposited (ALD) Al\textsubscript{2}O\textsubscript{3} and HfO\textsubscript{2} on In\textsubscript{x}Ga\textsubscript{1−x}As \((x=0, 0.15, 0.25,\) and 0.53). Using REELS, \(E_{g}\) values of the ALD-Al\textsubscript{2}O\textsubscript{3} and –HfO\textsubscript{2} were estimated to be 6.77 and 5.56 eV, respectively. The \(\Delta E_{v}\)'s were determined by measuring the core level to valence band maximum binding energy difference from the XPS spectra. The \(\Delta E_{c}\)'s were then extracted from \(\Delta E_{v}\)'s and the energy-band gaps of the oxides and In\textsubscript{x}Ga\textsubscript{1−x}As, and are in good agreement with those estimated from the Fowler–Nordheim tunneling. The \(\Delta E_{c}\)'s and \(\Delta E_{v}\)'s are larger than 1.5 and 2.5 eV, respectively, for all the ALD-oxide/In\textsubscript{x}Ga\textsubscript{1−x}As samples. © 2009 American Institute of Physics. [DOI: 10.1063/1.3078399]

III-V In\textsubscript{x}Ga\textsubscript{1−x}As metal-oxide-semiconductor field-effect-transistors (MOSFETS) with high \(\kappa\) dielectrics are now a strong contender for technologies beyond the 22–16 nm node complementary MOS due to the high electron mobility of In\textsubscript{x}Ga\textsubscript{1−x}As \((x=0\) to 0.53) 6–18 times of that of Si. Low interfacial densities of states \((D_{s})'s\) of less than \(<10^{12} \text{ eV}^{-1} \text{ cm}^{-2}\), small frequency dispersion, and low electrical leakage currents of \(<10^{-8} \text{ A/cm}^{2}\) with unpinned surface Fermi level, similar to those exhibited in the traditional SiO\textsubscript{2}/Si, are required for the high \(\kappa\) dielectrics on InGaAs. These properties have been attained in ultrahigh vacuum (UHV) deposited high \(\kappa\) Ga\textsubscript{2}O\textsubscript{3} (Ga\textsubscript{2}O\textsubscript{3}) \([\text{GGO}]\)\textsuperscript{12} and Ga\textsubscript{2}O\textsubscript{3}, \textsuperscript{3} and atomic layer deposited (ALD) Al\textsubscript{2}O\textsubscript{3} (Refs. 4 and 5) and HfO\textsubscript{2} (Refs. 6 and 7) on InGaAs without an interfacial layer. In\textsubscript{x}Ga\textsubscript{1−x}As MOSFETS have been successfully demonstrated with excellent device characteristics. \(4\textsuperscript{3–11}\) A capacitive effective thickness value of 1.0 nm has also been achieved in ALD-HfO\textsubscript{2} on In\textsubscript{0.53}Ga\textsubscript{0.47}As/InP. \(7\) Further, high-shaped stability of 850 °C has been achieved in Al\textsubscript{2}O\textsubscript{3}/GGO/InGaAs. \(12\)

In addition to low \(D_{s}\) small leakage currents, and device characteristics, energy-band parameters of high \(\kappa\) gate dielectrics/InGaAs, including oxide energy-band gaps \(E_{g}\), conduction-band offsets \(\Delta E_{c}\), and valence-band offsets \(\Delta E_{v}\) are essential for studying MOS device physics, design, and modeling. Several experimental techniques have been used to acquire these parameters: (1) x-ray photoelectron spectroscopy (XPS)\textsuperscript{13,14} for \(\Delta E_{v}\) determination; (2) internal photoemission spectroscopy\textsuperscript{15} and current-transport characteristics [Fowler–Nordheim (FN) tunneling]\textsuperscript{13,16} for \(\Delta E_{c}\) measurement; and (3) photoconductivity\textsuperscript{15} and electron energy loss spectroscopy (EELS) (Ref. 13) for \(E_{g}\) estimation.

The energy loss spectrum of O 1s core level (CL) photoelectron (also called XPS-EELS) is one of the commonly used EELS techniques to determine the \(E_{g}\) of oxide films (>2 nm).\textsuperscript{13} The relatively thick oxides were used to eliminate/reduce the signals from the oxide-semiconductor interface. However, the zero loss values may not be accurately determined if the O 1s peak consists of more than one component, such as the multipeaks presented in a mixed-oxide system and the hydroxide peaks appearing in an ALD-grown oxide, thus leading to the inaccuracy of the acquired \(E_{g}\) values. Furthermore, the imprecise determination of the \(E_{g}\) may occur if the energy loss spectrum of O 1s overlaps with other CL or Auger peaks. For instance, the Hf 4s CL peak of HfO\textsubscript{2} lies in the band-to-band transition region of O 1s XPS-EELS.

Fortunately, the above problems can be avoided by using reflection-EELS (REELS) due to the absence of CL and Auger electrons excitations in the low loss region. In addition, the inelastic scatterings, taking place within a few atomic layers (a mean free path of <2 nm) when a primary beam of low-energy (<500 eV) electrons was reflected from a solid surface, \textsuperscript{11} give the REELS signals. Thus, these inelastic scatterings enable an accurate determination of \(E_{g}\) of oxides with thickness down to 2 nm.

Therefore, in this work, we have combined REELS and XPS to accurately determine energy-band parameters of ultrathin ALD-Al\textsubscript{2}O\textsubscript{3} and –HfO\textsubscript{2} on In\textsubscript{x}Ga\textsubscript{1−x}As \((x=0, 0.15, 0.25,\) and 0.53). Particularly, synchrotron radiation source was employed for performing high-resolution (HR)-XPS. The energy-band parameters of UHV-GGO on GaAs were published earlier.\textsuperscript{16}

In\textsubscript{x}Ga\textsubscript{1−x}As \((x=0, 0.15, 0.25)\) and In\textsubscript{0.53}Ga\textsubscript{0.47}As epilayers with Si-doping of \(5 \times 10^{17} \text{ cm}^{-3}\) were molecular beam epitaxy–grown on 2 in. Si-doped GaAs and InP substrates of \(2 \times 10^{18} \text{ cm}^{-3}\), respectively. The growth of ALD-Al\textsubscript{2}O\textsubscript{3} (Ref. 5) and ALD-HfO\textsubscript{2} (Ref. 6) on InGaAs was discussed earlier.

The HR-XPS were taken at the U5 undulator beam-line of National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Photoelectrons were detected at a take-off angle of 53° with respect to the surface sample by a PHI 2794 mm diameter hemispherical electron analyzer. REELS measurements were performed by using SPECS PHOIBOS 150

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hemispherical energy analyzer at a constant pass energy mode with a pass energy of 3 eV and a primary electron energy of 400 eV. The full width at half maximum of the elastic scattering peak (zero loss) was ~0.54 eV.

\[ \Delta E_v = (E_{\text{CL}}^{\text{InGaAs}} - E_{\text{VBM}}^{\text{InGaAs}}) - (E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}}) + \Delta E_{\text{CL}}. \]

where $E_{\text{CL}}$ and $E_{\text{VBM}}$ are the binding energy of CL and VBM, and $(E_{\text{CL}}^{\text{InGaAs}} - E_{\text{VBM}}^{\text{InGaAs}})$ and $(E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}})$ are the binding energy differences of CL to VBM for InGaAs and oxides, respectively. The last term $\Delta E_{\text{CL}}$ is the energy separation between the CL of oxides and that of semiconductors across the oxides/InGaAs interface.

The experiments on each of the following steps were carefully and thoroughly carried out: (i) acquisition of the VBM and As 3d CL spectra of the sputter-cleaned In$_{x}$Ga$_{1-x}$As ($x=0$, 0.15, 0.25, and 0.53) surface prior to oxide deposition for $(E_{\text{CL}}^{\text{InGaAs}} - E_{\text{VBM}}^{\text{InGaAs}})$ (the VBM values were determined from the intersection of a line fit to the leading edge of the valence band spectrum with the background level); (ii) attainment of the Al 2p and Hf 4f CL spectra along with the corresponding VBM of the Al$_2$O$_3$ and HfO$_2$ films after the deposition of oxides for $(E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}})$; and (iii) determination of the energy separation $\Delta E_{\text{CL}}$ across the Al$_2$O$_3$/In$_x$Ga$_{1-x}$As and HfO$_2$/In$_x$Ga$_{1-x}$As interface. Note that some oxides with thicknesses of >3 nm were thinned down by sputtering, while no sputtering was needed for thinner oxides.

Figures 1(a) and 1(b) illustrate the As 3d, Al 2p, and Hf 4f CL along with the VBM of ALD-Al$_2$O$_3$ and ALD-HfO$_2$ on GaAs with incident photon energies of 680 eV. The same analytical methods were also carried out to investigate the $\Delta E_v$ of Al$_2$O$_3$ and HfO$_2$ grown on In$_x$Ga$_{1-x}$As with different indium (In) contents. The experimental values are summarized in Table I.

The $E_v$ values of the high $\kappa$ materials were estimated from the REELS spectrum using the onsets of band-to-band transition (valence-electron excitation for single particles) for the zero loss (elastic scattering) peaks. Figure 2 shows the REELS spectra for SiO$_2$, Al$_2$O$_3$, and HfO$_2$ thin films with a primary energy of 400 eV. The elastic peaks were normalized to the same area. The $E_v$ value of SiO$_2$ appears at ~8.9 ± 0.05 eV, which is in good agreement with the commonly obtained value of 8.8–9.0 eV, demonstrating the validity of our REELS measurement. The bulk plasmon peaks were located at ~22.5, ~22.1, and ~14.5 eV for SiO$_2$, Al$_2$O$_3$, and HfO$_2$, respectively. Experimental data of $E_v$ values were 6.77 ± 0.05 and 5.56 ± 0.05 eV for Al$_2$O$_3$ and HfO$_2$, respectively. These results are consistent with those from REELS analyses reported on Al$_2$O$_3$ and HfO$_2$.

In addition, the impurity content in the films, such as residual carbon and nitrogen, was less than 1 at. % by the XPS analyses (not shown).

Combining the experimental data of $\Delta E_v$ and the oxide $E_v$ with the band gap values of In$_x$Ga$_{1-x}$As ($x=0$, 0.15, 0.25, and 0.53), the conduction band offsets ($\Delta E_v$) important energy-band parameters for MOS devices, can be simply derived from the following equation:

\[ \Delta E_v = E_v(\text{oxide}) - E_v(\text{InGaAs}) - \Delta E_v. \]

The energy-band parameters of ALD-oxides/InGaAs heterostructures are summarized in Fig. 3. Note that the $\Delta E_v$ and $\Delta E_v$ of ALD-Al$_2$O$_3$ and HfO$_2$/In$_x$Ga$_{1-x}$As increase as $x$ varies from 0 to 0.53. The lattice parameters of the strained In$_x$Ga$_{1-x}$As layers have been obtained through thorough high-resolution x-ray diffraction measurements using synchrotron radiation. The value of $x$ was then determined with an accuracy of 3%–5%. The samples after XRD were then used to calibrate the In/Ga ratio studied using in situ XPS. The parameters of CL and VBM energy difference of Table I. Parameters of CL and VBM energy difference of (i) $E_{\text{CL}}^{\text{InGaAs}} - E_{\text{VBM}}^{\text{InGaAs}}$, (ii) $E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}}$, (iii) $E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}}$ for the ALD-Al$_2$O$_3$ and (iv) $E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}}$, (v) $E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}}$, and (vi) $E_{\text{CL}}^{\text{oxide}} - E_{\text{VBM}}^{\text{oxide}}$ for HfO$_2$ grown on In$_x$Ga$_{1-x}$As along with the corresponding estimated values of $E_v$. 

![Image](https://via.placeholder.com/150)
ou reports layers were achieved by using optical measurement in previous HR-XPS and REELS for acquiring the band parameters of thickness. These, thus, have proved the uniqueness of using a range of oxide thickness varying from 3 to 8 nm with the band parameters presented here were obtained from a wide 0.75 eV for unstrained In$_{0.53}$Ga$_{0.47}$As on InP were used in our calculation. The derived $\Delta E_c$ values are consistent with those determined using FN tunneling analysis. Moreover, the band parameters presented here were obtained from a wide range of oxide thickness varying from 3 to 8 nm with the same/similar energy-band values regardless of the oxide thickness. These, thus, have proved the uniqueness of using HR-XPS and REELS for acquiring the band parameters of ultrathin oxide films on semiconductors. In contrast, it is difficult, if not impossible, in utilizing electrical transport analysis, such as FN tunneling, to derive $\Delta E_c$ for the oxide thickness of less than 4 nm due to the direct tunneling effect.

In conclusion, energy-band offsets ($\Delta E_c$, $\Delta E_v$) and energy-band gaps of the ALD-Al$_2$O$_3$ and –HfO$_2$/In$_{0.53}$Ga$_{0.47}$As ($x$=0, 0.15, 0.25, and 0.53) were obtained through thorough and systematic HR-XPS and REELS analyses. The band offsets of both the ALD-Al$_2$O$_3$ and –HfO$_2$ on InGaAs are adequate for reliable gate dielectric operation. The $\Delta E_c$ values obtained from the HR-XPS and REELS analyses are in good agreement with those estimated from the electrical measurement of FN tunneling. The results are valuable for further understanding and modeling of the III-MOS devices.

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![FIG. 2. (Color online) Reflection electron energy loss spectra for ALD-HfO$_2$, ALD-Al$_2$O$_3$, and SiO$_2$ thin films at the primary energy of 400 eV.](image1)

![FIG. 3. (Color online) Energy-band parameters for (a) Al$_2$O$_3$/In$_{1-x}$Ga$_x$As and (b) HfO$_2$/In$_{1-x}$Ga$_x$As heterostructures acquired by using HR-XPS and REELS.](image2)