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Energy barriers at interfaces between (100) In$_x$Ga$_{1-x}$As (0 ≤ x ≤ 0.53) and atomic-layer deposited Al$_2$O$_3$ and HfO$_2$

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I. M. Povey,$^3$ M. E. Pembble,$^3$ E. O’Connor,$^3$ P. K. Hurley,$^3$ and S. B. Newcomb$^4$

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The electron energy band alignment at interfaces of In$_{x}$Ga$_{1-x}$As (0 ≤ x ≤ 0.53) with atomic-layer deposited insulators Al$_2$O$_3$ and HfO$_2$ is characterized using internal photoemission and photoconductivity experiments. The energy of the In$_{x}$Ga$_{1-x}$As valence band top is found to be only marginally influenced by the semiconductor composition. This result suggests that the known bandgap narrowing from 1.42 to 0.75 eV when the In content increases from 0 to 0.53 occurs mostly through downshift of the semiconductor conduction band bottom. It finds support from both electron and hole photoemission data. Similarly to the GaAs case, electron states originating from the interfacial oxidation of In$_{x}$Ga$_{1-x}$As lead to reduction in the electron barrier at the semiconductor/oxide interface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3137187]

The In$_{x}$Ga$_{1-x}$As semiconducting alloys with their known superb high-frequency performance are the leading contenders to replace Si in high-speed metal-insulator-semiconductor (MIS) devices. The key requirement for the gate stack is a high barrier for electrons and holes in the semiconductor, which would need large band offsets at MIS interfaces. Yet, there is significant uncertainty regarding band offset values at the interfaces of In$_{x}$Ga$_{1-x}$As with oxides: Over seemingly identically fabricated In$_{0.53}$Ga$_{0.47}$As/HfO$_2$ structures a variation in the valence band (VB) offset up to 0.5 eV is reported,$^{1,2}$ which substantially exceeds the ∼0.3 eV VB shift between GaAs and In$_{0.53}$Ga$_{0.47}$As recently reported for the interface with HfO$_2$. This uncertainty (confusion) is likely caused by the insulator charging. An additional problem is associated with incorporation of In into the “native” oxide interlayer (IL) formed when depositing the insulator, which may cause significant reduction of the interface barrier height as, for instance, is observed at interfaces of Ge and GaAs with Al$_2$O$_3$ and HfO$_2$.\textsuperscript{3,5,6}

Here we report on band offsets at the interfaces between In$_{x}$Ga$_{1-x}$As (x ≤ 0.53) and atomic-layer deposited (ALD) Al$_2$O$_3$ and HfO$_2$ as measured by internal photoemission (IPE) and photoconductivity (PC) spectroscopy. The narrowing of the In$_{x}$Ga$_{1-x}$As gap with increasing In content is found to occur mainly through a downshift of the In$_{x}$Ga$_{1-x}$As conduction band (CB) edge while the VB top remains at the same energy within an accuracy of 0.1 eV.

Samples were prepared on n-In$_{x}$Ga$_{1-x}$As [n$_D$ ≈ (1–5) × 10$^{17}$ cm$^{-3}$] layers grown epitaxially on (100)GaAs (x = 0, 0.15, 0.30) or on (100)InP (x = 0.53). We compared 10 nm thick ALD films of Al$_2$O$_3$ [Al(CH$_3$)$_2$]+H$_2$O precursors at 300 °C to 10–24 nm thick HfO$_2$ films [HfCl$_4$+H$_2$O or Hf[N(CH$_3$)$_2$)$_2$]+H$_2$O precursors at 300 or 250 °C, respectively] (in ALD the metal precursor pulse was injected first). These oxides exhibit distinctly different interface morphology when deposited on In$_{0.53}$Ga$_{0.47}$As. Transmission electron microscopy (TEM) finds no IL at the In$_{0.53}$Ga$_{0.47}$As/Al$_2$O$_3$ interface, while a ∼1 nm thick IL is seen in the In$_{0.53}$Ga$_{0.47}$As/HfO$_2$ samples (cf. Fig. 1). Apparently, during ALD of Al$_2$O$_3$ the residual As oxides are removed while In and Ga oxides are dissolved in alumina, as suggested by TEM images revealing a ∼3 nm thick alumina layer with a higher density, and by the results of time-of-flight mass spectrometry (not shown) indicating the presence of an intermixed interfacial region comprised of In, Ga, and Al oxides. The band alignment at the In$_{x}$Ga$_{1-x}$As interfaces was determined using measurements of IPE and PC at room temperature on MIS capacitors formed by evaporation of transparent Au or Al electrodes on the top of Al$_2$O$_3$ and HfO$_2$ layers. The oxide gap width and the electron and hole barrier heights are obtained from the spectral thresholds of the PC and IPE quantum yield (Y) defined in terms of photocurrent per incident photon.\textsuperscript{7,8}

Logarithmic plots of the yield Y are shown in Fig. 2 for MIS capacitors with 10 nm thick Al$_2$O$_3$ (a) and HfO$_2$ (b) thicknesses. The electron photoemission data are presented in Fig. 3 for In$_{x}$Ga$_{1-x}$As/HfO$_2$ structures. The narrow-
insulators deposited on epitaxial In_{0.53}Ga_{0.47}As layers grown on InP as measured under different positive (open circles) and negative (filled circles) bias applied to the Au top electrode. In the photon energy range $h\nu<5.5$ eV the dominant contribution to the photocurrent measured under positive bias stems from electron IPE from the In_{x}Ga_{1-x}As VB to the oxide CB. This is suggested by the absence of a comparable photocurrent when the metal is biased negative as well as by modulation of the IPE spectra at photon energies of 2.6–2.8 eV ($E_1$, $E_1+\Delta_1$), 4.5 eV ($E'_1$) and 4.7 eV ($E_2$) in Fig. 2 corresponding to excitation of direct optical transitions in In_{0.53}Ga_{0.47}As.\(^9\)\(^-\)\(^12\) At higher photon energies the photocurrents measured under positive and negative metal bias become close and exhibit the same spectral distribution, suggesting that the signal is due to the intrinsic oxide PC. This allows one to infer the bandgap ($E_g$) of Al$_2$O$_3$ and HfO$_2$, found to be equal to 6.1±0.1 eV, typical of low-temperature deposited alumina,\(^7\) and 5.6/5.9±0.1 eV, respectively (cf. arrows in Fig. 2). In the In$_{0.53}$Ga$_{0.47}$As/HfO$_2$ sample the IL-assisted electron injection becomes more pronounced with increasing positive bias resulting in an additional “low” threshold.\(^6\) The yield measured under negative bias in this sample is enhanced near $E_2\approx 4.7$ eV, suggesting hole IPE from the In$_{0.53}$Ga$_{0.47}$As into HfO$_2$ and enabling determination of the barrier height between the top of the oxide VB and the bottom of CB in In$_{0.53}$Ga$_{0.47}$As, which is equal to 3.2±0.2 eV.

To monitor the energy of the In$_{0.53}$Ga$_{0.47}$As VB as a function of In content, quantum yield spectra have been measured, as illustrated in Fig. 3, for MIS capacitors with Al$_2$O$_3$ (a) and HfO$_2$ (b) insulators deposited on In$_{x}$Ga$_{1-x}$As with different In concentration. The curves shown are measured under positive bias corresponding to an average strength of the electric field in the oxide ($F$) of 2 and 1.5 MV/cm for the Al$_2$O$_3$ and HfO$_2$ insulators, respectively. The important finding here is that the increase in the In fraction from 0 to 0.53 does not lead to any substantial spectral shift in the IPE curves within the error margins (0.07–0.1 eV) indicated by arrows. In the case of Al$_2$O$_3$ (Fig. 3(a)), the yield of direct electron IPE into the alumina CB (3.5<$h\nu$<5.5 eV) becomes higher in the In-containing samples compared to the pure GaAs, which is consistent with “dissolution” of the “native” oxide IL in Al$_2$O$_3$ as revealed by TEM. Nevertheless, the IL-assisted IPE is not completely eliminated.

Spectral thresholds of electron and hole IPE were obtained from $Y^{1/3}$-$h\nu$ and $Y^{1/2}$-$h\nu$ plots, respectively, as exemplified for an In$_{0.15}$Ga$_{0.85}$As/Al$_2$O$_3$ sample in Fig. 4 by $Y^{1/3}$-$h\nu$ plots measured under incrementally enhanced positive metal bias. The plots reveal two contributions to the electron IPE; The direct IPE from the VB of In$_{x}$Ga$_{1-x}$As into
the oxide CB characterized by the “high” IPE threshold [\(\Phi(\text{high})\)] and the IL-assisted IPE with the “low” [\(\Phi(\text{low})\)] barrier.8 Values of these barriers measured in samples with different In content are shown in Figs. 5(a) and 5(b) as functions of applied electric field. These Schottky plots were used to determine the zero-field barrier height corresponding to the band offset at the In\(_{x}\)Ga\(_{1-x}\)As/oxide interface (unaffected by the image-force effect). In the Al\(_2\)O\(_3\)-samples the barriers for both direct IPE into the oxide CB and for the IL-mediated transitions are insensitive to the In content within an accuracy of 0.1 eV, importantly indicating that (a) the energy of the semiconductor VB top remains fixed at 3.45 ± 0.10 eV below the alumina CB bottom and, (b) the possible presence of In in the near-interfacial oxide does not lead to additional barrier lowering.

In the case of HfO\(_2\) the barrier between the top of the In\(_{x}\)Ga\(_{1-x}\)As VB and the bottom of the oxide CB is 3.35 ± 0.10 eV and, like in the case of Al\(_2\)O\(_3\), shows little sensitivity to the In content. Consistent with this result, the hole IPE threshold at the In\(_{x}\)Ga\(_{1-x}\)As/HfO\(_2\) interface is found at 3.2 ± 0.2 eV as compared to 3.8 ± 0.2 eV in GaAs/HfO\(_2\), indicating a downshift of the semiconductor CB bottom with increasing In content. By contrast, the observed spread in the low spectral threshold values corresponding to the IL-assisted electron IPE into HfO\(_2\) may be caused by the different thickness of the IL and/or its composition. This is suggested by differences in the \(\Phi(\text{low})\) values observed in samples with HfO\(_2\) layers deposited from different Hf precursors [cf. symbols \(\bigtriangleup\) and \(\bigtriangledown\) in Fig. 5(b) corresponding to ALD from HfCl\(_4\)+H\(_2\)O and Hf[\(\text{N}3\text{CH}2\text{CHRI}\)]\(_3\)+H\(_2\)O, respectively]. Changes in the IL-related barrier would also explain the earlier reported sensitivity of IPE in GaAs/Al\(_2\)O\(_3\) entities to the semiconductor surface preparation.13 At the same time, the barrier \(\Phi(\text{high})\), corresponding to direct electron IPE into the oxide CB, appears to be insensitive to the HfO\(_2\) deposition process [cf. Fig. 5(a)] affirming its fundamental character.

As a final step, the fundamental CB (\(\Delta E_c\)) and VB (\(\Delta E_v\)) offsets at the interfaces of In\(_{x}\)Ga\(_{1-x}\)As with Al\(_2\)O\(_3\) and HfO\(_2\) were calculated from the measured barrier between the semiconductor VB and the oxide CB, combined with the oxide bandgap width. We have found that the top of the In\(_{x}\)Ga\(_{1-x}\)As VB remains at the same energy below the Al\(_2\)O\(_3\) CB (3.45 ± 0.10 eV) and HfO\(_2\) CB (3.35 ± 0.10 eV) when the In content \(x\) increases from 0 to 0.53. This corresponds to a CB offset increase from approximately 2 eV for GaAs to 2.7 eV for In\(_{0.53}\)Ga\(_{0.47}\)As (cf. inset in Fig. 4), promising an improvement in the gate insulation. This result is consistent with the band offsets observed in strained GaAs/In\(_{x}\)Ga\(_{1-x}\)As quantum well structures where the CB offset accounts for 85% of the bandgap difference.10 Calculations based on the charge neutrality concept also suggest that the VBs of GaAs and InAs are aligned at their interfaces with HfO\(_2\) (the “common anion” case),15 making it also unlikely that the VB top energy would vary at the interfaces of In\(_{x}\)Ga\(_{1-x}\)As with the same oxide. Like at the interfaces of GaAs with the currently studied oxides,6 the oxide IL formed during the ALD process provides a lower electron barrier, but this barrier reduction is insensitive to the In content in the semiconductor, suggesting that the narrow-gap In\(_2\)O\(_3\) phase is not formed during ALD.

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