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Energy barriers at interfaces of (100)GaAs with atomic layer deposited Al$_2$O$_3$ and HfO$_2$

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Band alignment at the interfaces of (100)GaAs with Al$_2$O$_3$ and HfO$_2$ grown using atomic layer deposition is determined using internal photoemission and photocconductivity measurements. Though the inferred conduction and valence band offsets for both insulators were found to be close to or larger than 2 eV, the interlayer grown by concomitant oxidation of GaAs reduces the barrier for electrons by approximately 1 eV. The latter may pose significant problems associated with electron injection from GaAs into the oxide. © 2008 American Institute of Physics. DOI: 10.1063/1.3021374

The atomic layer deposition (ALD) is a promising method to fabricate insulators on high-mobility other semiconductors (Ge, GaAs, In$_x$Ga$_{1-x}$As, etc.). Because the ALD exposes the surface to a large amount of oxidant, formation of an oxide can hardly be avoided. The oxides on GaAs and In$_x$Ga$_{1-x}$As are known to be poor insulators, with the band-gap ($E_g$) of Ga$_2$O$_3$ being only 4 eV wide, i.e., much smaller than the gaps of most frequently used ALD insulators, i.e., Al$_2$O$_3$ ($E_g$ = 6.0–6.2 eV) and HfO$_2$ ($E_g$ = 5.6–5.9 eV). Therefore, formation of an oxide interlayer (IL) may lead to low interface energy barriers and high leakage current, as long known for anodic oxide on GaAs. Recently, low energy barriers have been reported between the GaAs valence band (VB) and the conduction band (CB) of HfO$_2$ grown using the atomic beam technique or ALD Al$_2$O$_3$; the inferred barriers of 2.5 eV or less at an electric field of 1 MV/cm leave only ~1 eV CB offsets—clearly insufficient for reliable insulation. However, a similar 2.3 eV low barrier was found earlier for Ga$_2$O$_3$/Ga$_2$O$_3$ stacks on GaAs, which was associated with the narrow-gap Ga$_2$O$_3$ IL, suggesting that oxidation of GaAs might be the reason for the low barriers reported in Refs. 5 and 6. In this work by analyzing the (100)GaAs interfaces with ALD Al$_2$O$_3$ and HfO$_2$ layers with different ILs, we separated the energy barriers associated with electron states of the high-$\kappa$ oxides and those of the IL, explaining observations made in Refs. 5 and 6.

Studied samples were prepared on (100)GaAs n- or p-type ($n_{d},n_{i} = 10^{17}$ cm$^{-3}$) single crystals. To examine the effect of the IL, various combinations of surface cleaning and ALD growth were used. First, after HCl surface cleaning a 10 nm thick amorphous Al$_2$O$_3$ layer was grown at 300 °C either by plasma ALD from Al(CH$_3$)$_3$ and O$_2$ precursors or using thermal ALD from Al(CH$_3$)$_3$ and H$_2$O. The oxygen plasma in the former recipe is expected to lead to the thickest GaAs oxide IL. Second, ALD from HfCl$_4$ and H$_2$O precursors at 300 °C was used to grow 10 nm thick polycrystalline HfO$_2$ on HCl-cleaned GaAs. To obtain a thicker GaAs oxide, the HCl pre-ALD clean was omitted in some samples. Third, ~10 nm thick ALD HfO$_2$ was grown from Hf[N(CH$_3$)$_2$]$_4$, and H$_2$O precursors at 250 °C on GaAs surfaces covered with native oxide. The IL was analyzed using cross-sectional transmission electron microscopy (TEM) and spectroscopic ellipsometry (SE) in the range $h\nu$=1.6–6.0 eV. In the GaAs/HfO$_2$ samples TEM reveals an oxide IL of 0.9 nm thickness in both types of samples grown from HfCl$_4$ [cf. Fig. 1(a)], although SE suggests a slightly thinner IL in the HCl-pre-cleaned sample (0.6 nm) as compared to the 0.8–0.9 nm thick one found if the clean was omitted. This discrepancy can be explained by a nonuniform IL: in some TEM images it reaches 1.4 nm. Both TEM and SE find the same 1.8 nm thick IL in samples grown from Hf[N(CH$_3$)$_2$]$_4$ and H$_2$O [cf. Fig. 1(b)], which is consistent with the earlier report. In the GaAs/Al$_2$O$_3$ samples the IL thickness was estimated from the SE spectra as ~0.5 and 2.5 nm for the thermally and plasma-assisted ALD oxide growth, respectively. TEM indicates the same trend with slightly different IL thicknesses of ~1.0 and 2–3 nm, respectively.

Capacitors were formed by evaporating semitransparent (15 nm thick) Au or Al electrodes of 0.5 mm$^2$ area on top of the ALD oxide. These capacitors were used to determine the interface band alignment through observations of internal photoemission (IPE) of electrons excited from GaAs into the

![FIG. 1. TEM images of the (100)GaAs/HfO$_2$ interface in samples prepared by thermal ALD of HfO$_2$ from HfCl$_4$ and H$_2$O precursors on HCl-etched GaAs (a) and from Hf[N(CH$_3$)$_2$]$_4$ and H$_2$O on the pristine GaAs surface (b). The arrows indicate the thicknesses of the HfO$_2$ of the IL between HfO$_2$ and GaAs.](image-url)
oxide and oxide photoconductivity (PC) in the range $\hbar \nu = 1.8 - 6.5$ eV.\(^3\) The quantum yield ($Y$) is defined as the photocurrent normalized to the incident photon flux.\(^9\)

Logarithmic plots of the IPE/PC spectra in plasma (●) and thermal ALD Al\(_2\)O\(_3\) samples (○) are shown in Figs. 2(a) and 2(b), respectively, measured for different positive and negative voltages $V_\nu$ applied to the top Au electrode, respectively. In both types of samples the current observed under positive bias is much higher than that under the negative one, pointing to electron IPE at the GaAs/Al\(_2\)O\(_3\) interface. At the energies corresponding to excitation of direct optical transitions in the GaAs crystal (Γ\(_{8}\)→Γ\(_{7}\) at $E_\nu=4.4$ eV and X\(_7\)-X\(_8\)/Σ\(_{7}\)-Σ\(_{8}\) at $E_\nu=4.9$ eV at 300 K as observed with electroreflectance\(^10\)), the yield deviates from the monotonic increase with $\hbar \nu$ indicating GaAs as the source of photoelectrons.\(^9\) The latter is supported by the observation of nearly identical spectra under positive bias in Au- and Al-gated samples. In the plasma-grown Al\(_2\)O\(_3\) sample (●) the electron IPE quantum yield (positive bias) is reduced compared to the thermal ALD case, which is consistent with stronger electron scattering in a thicker IL. Variations in the alumina ALD process are also seen to affect the yield under negative bias [cf. Fig. 2(b)]; in the plasma-grown sample (●) the onset of the photocurrent is shifted to $\sim$4 eV compared to $\sim$5 eV for the thermal ALD sample (○). The former value is close to the bandgap $E_g$(Ga\(_2\)O\(_3\))=4.0 eV,\(^2\) suggesting PC excitation in the GaAs oxide IL, although the spectrum is broadened, possibly due to the presence of some amount of As or Ga suboxides. In the range $\hbar \nu > 5.5$ eV the spectral curves at both bias polarities converge, indicating excitation of intrinsic PC in Al\(_2\)O\(_3\) with an energy threshold of $E_g$(Al\(_2\)O\(_3\))=6.1 eV, marked by arrows in Fig. 2.

The IPE/PC spectra of samples with thermal ALD HfO\(_2\) (HCl\(_2\) and H\(_2\)O) on the native oxide covered (●) or the HCl-cleaned GaAs (○) are shown in Fig. 3. Panels (a) and (b) correspond to measurements under $V_\nu=+2$ V and negative biases of $-1$, $-2$, $-3$ V. The results for the samples with the thickest IL, i.e., grown from Hf[CH\(_2\)]\(_4\) and H\(_2\)O on the native GaAs oxide, under $+2$ or $-2$ V bias are also shown (●) in panels (a) and (b), respectively. Compared to negative bias data, the enhanced photocurrent under positive bias can again be assigned to electron IPE from GaAs as the spectral features $E_0'$ and $E_2$ clearly emerge. The sample with a predeposition native oxide remaining (● Fig. 3(a)) shows additional photocurrent in the low photon energy range ($\hbar \nu < 3$ eV) modulated with another direct transition in GaAs $[\Lambda_2^+\Lambda_1^-$ at $E_1=2.9$ eV at 300 K (Ref. 9)], indicating electron IPE from GaAs into the IL. Thus, a thicker IL leads to a
substantial reduction of the electron IPE threshold. Moreover, in the sample with the thickest IL (Hf[N(CH3)2]4 + H2O ALD, \(\square\) in Fig. 3), the photocurrent spectra become nearly identical under opposite field orientations and lose the signatures of direct transitions in GaAs. This behavior would be consistent with the optical excitation inside the IL.

The influence of direct optical transitions can also be noticed in the spectra measured under negative bias \(\square\) [panel (b)], suggesting IPE of holes from GaAs into HfO2. However, as compared to electron IPE \(\square\) [panel (a)], the character of yield variation is reversed: the yield is suppressed when exciting \(\Gamma_{X}^{p} \Gamma_{X}^{p}\) at \(E_{0}^{e}=4.4\) eV but increases for the \(X_{7}^{-}\) excitation at \(E_{2}=4.9\) eV, which allows one to allocate the energy of electrons and holes in the final state of these transitions to the HfO2 bandgap edges: the final energy of a photohole in the GaAs VB is insufficient for over-barrier injection into the oxide VB in the first case but sufficient in the case of the \(X_{7}^{-}\) excitation. The spectral threshold of hole IPE from the CB of GaAs into the VB of HfO2 was evaluated from the \(Y^{1/3}\) plots shown in the inset in Fig. 3(b) to be close to \(\Phi_{h}(\text{HfO2}) = 3.8 \pm 0.2\) eV. The sample with the thickest IL \(\square\) in Fig. 3] exhibits nearly the same IPE/PC spectra under opposite bias polarities, suggestive of PC excitation. No optical singularities of GaAs are prominently reflected by the photocurrent spectra. At higher photon energy \((h\nu > 5\) eV) the spectral curves measured in different samples converge, indicating excitation of intrinsic PC in HfO2 with threshold \(E_{s}(\text{HfO2})=5.6\) eV, marked by arrows in Fig. 3.

Spectral thresholds of electron IPE were found using \(Y^{1/3}\) plots shown for the samples with thermal ALD Al2O3 and HfO2 (HCl-cleaned sample) insulators in Figs. 4(a) and 4(b), respectively. The inferred IPE thresholds only weakly depend on the applied voltage \(V_{b}\), as illustrated by the Schottky plot in the inset in Fig. 4(a), in which the strength of electric field was calculated by dividing the applied voltage \(V_{b}\) by the oxide stack thickness \(d\). This is also true for the samples with plasma-assisted ALD Al2O3 (curves not shown) and HfO2 deposited on the unetched GaAs \(\square\) in Fig. 4]. Extrapolation to zero field yields the barrier height between the GaAs VB and the CB of Al2O3 at \(\Phi_{h}(\text{Al2O3}) =3.4 \pm 0.1\) eV, which corresponds to a CB offset of 2.0 eV. Samples with a HfO2 insulator also exhibit nearly field-independent IPE threshold of \(\Phi_{h}(\text{HfO2})=3.3 \pm 0.1\) eV, yielding a comfortably large CB offset of 1.9 eV. The sample without HCl clean shows a lower threshold \(\Phi_{h}(\text{IL}) = 2.3 \pm 0.1\) eV, which is close to the previously reported threshold for electron IPE from the GaAs VB into the CB of the Ga2O3 IL in GaAs/Ga2O3/GaOx structures as well as to the spectral threshold found for atomic-beam grown HfO2 on GaAs.

To conclude, we found both HfO2 and Al2O3 to provide CB and VB offsets at their interfaces with GaAs of around 2 eV, which make these material suitable for gate insulation. The problem actually resides with the IL providing only a 0.9 eV CB offset at the interface: formation of such IL due to oxidation of GaAs in the course of high-\(\kappa\) oxide deposition may lead to enhanced charge injection from GaAs into the insulating stack. Therefore, the growth of a GaAs oxide IL of any substantial thickness appears undesirable, mandating either growth of a non-oxide passivating layer, use of a gate oxide deposition without a large oxidant supply, or, else,

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