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Energy barriers at interfaces of (100)GaAs with atomic layer deposited Al_2O_3 and HfO_2

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Band alignment at the interfaces of (100)GaAs with Al_2O_3 and HfO_2 grown using atomic layer deposition is determined using internal photoemission and photoconductivity 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.

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The atomic layer deposition (ALD) is a promising method to fabricate insulators on high-mobility other semiconductors (Ge, GaAs, $\text{In}_x\text{Ga}_{1-x}\text{As}$, etc.).¹ 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 $\text{In}_x\text{Ga}_{1-x}\text{As}$ are known to be poor insulators, with the band-gap (E_g) of Ga_2O_3 being only 4 eV wide,^{2,3} i.e., much smaller than the gaps of most frequently used ALD insulators, i.e., Al_2O_3 ($E_g=6.0\text{--}6.2$ 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.⁴ 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 technique⁵ or ALD Al_2O_3 :⁶ 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 $\text{Ga}_2\text{O}_3/\text{GaGdO}_x$ stacks on GaAs, which was associated with the narrow-gap Ga_2O_3 IL,⁷ 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_2O_3 and HfO_2 layers with different ILs, we separated the energy barriers associated with electron states of the high- κ 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 ($n_d, n_a \approx 10^{17}$ 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_2O_3 layer was grown at 300 °C either by plasma ALD from $\text{Al}(\text{CH}_3)_3$ and O_2 precursors or using thermal ALD from $\text{Al}(\text{CH}_3)_3$ and H_2O . The oxygen plasma in the former recipe is expected to lead to the thickest GaAs oxide IL. Second, ALD from HfCl_4 and H_2O 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 $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ and H_2O 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 $h\nu=1.6\text{--}6.0$ 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 $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ and H_2O [cf. Fig. 1(b)], which is consistent with the earlier report.⁸ In the GaAs/ Al_2O_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 mm² 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

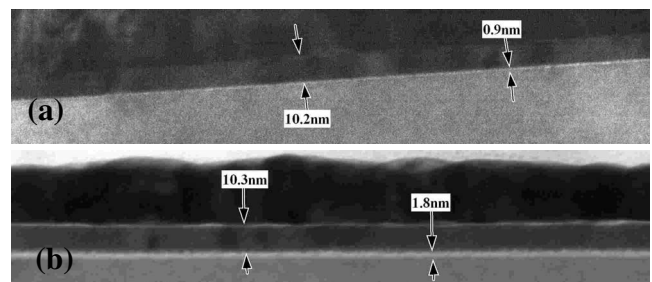


FIG. 1. TEM images of the (100)GaAs/ HfO_2 interface in samples prepared by thermal ALD of HfO_2 from HfCl_4 and H_2O precursors on HCl-etched GaAs (a) and from $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$ and H_2O on the pristine GaAs surface (b). The arrows indicate the thicknesses of the HfO_2 of the IL between HfO_2 and GaAs.

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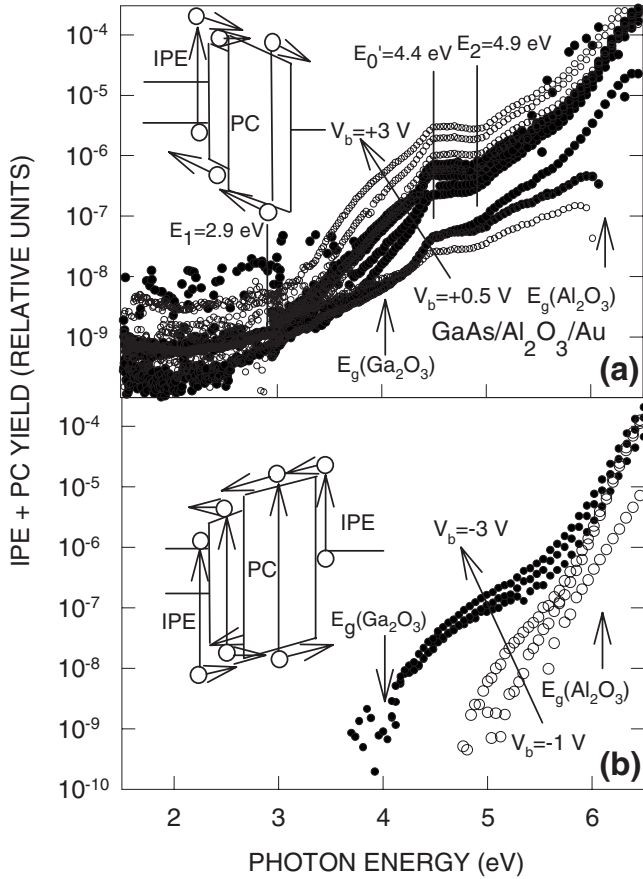


FIG. 2. IPE+PC yield as a function of photon energy in (100)GaAs/Al₂O₃(10 nm)/Au samples with plasma-assisted (●) and thermal ALD oxides (○) measured under positive bias (a) of 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, or 3.0 V, or negative bias (b) of -1, -2, or -3 V applied to the Au electrode. The vertical lines indicate energies of optical singularities in GaAs; vertical arrows mark thresholds of intrinsic PC in Al₂O₃ and Ga₂O₃. The insets show schematics of electron transitions.

oxide and oxide photoconductivity (PC) in the range $h\nu = 1.8\text{--}6.5$ 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 Al₂O₃ samples (○) are shown in Figs. 2(a) and 2(b), respectively, measured for different positive and negative voltages V_b 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/Al₂O₃ interface. At the energies corresponding to excitation of direct optical transitions in the GaAs crystal ($\Gamma_8^v\text{--}\Gamma_7^c$ at $E_0' = 4.4$ eV and $X_7\text{--}X_6/\Sigma_v\text{--}\Sigma_c$ at $E_2 = 4.9$ eV at 300 K as observed with electroreflectance¹⁰), the yield deviates from the monotonic increase with $h\nu$ 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 Al₂O₃ 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 ~ 4 eV compared to ~ 5 eV for the thermal ALD sample (○). The former value is close to the bandgap $E_g(\text{Ga}_2\text{O}_3) = 4.0$ eV,² suggest-

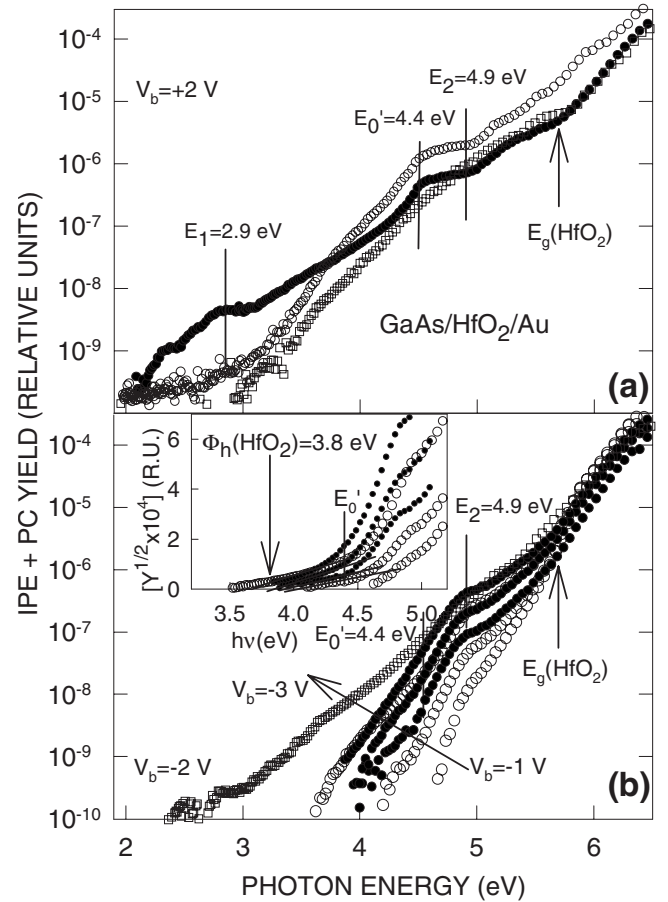


FIG. 3. IPE+PC yield as a function of photon energy measured on (100)GaAs/HfO₂(10 nm)/Au samples with HfO₂ layers deposited from HfCl₄ and H₂O without (●) and with pre-ALD HCl surface clean (○) measured under positive (a) 2 V bias and negative bias (b) of -1, -2, or -3 V on the Au electrode. The spectra (□) taken at +2 and -2 V biases on samples with 15 nm thick HfO₂ grown at 250 °C from Hf[N(CH₃)₂]₄ and H₂O are shown for comparison. The inset illustrates determination of the hole $\Phi_h(\text{HfO}_2) = 3.8$ eV. The vertical lines indicate energies of optical singularities in GaAs, while vertical arrows show the threshold of intrinsic PC in HfO₂.

ing 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 $h\nu > 5.5$ eV the spectral curves at both bias polarities converge, indicating excitation of intrinsic PC in Al₂O₃ with an energy threshold of $E_g(\text{Al}_2\text{O}_3) = 6.1$ eV, marked by arrows in Fig. 2.

The IPE/PC spectra of samples with thermal ALD HfO₂ (HfCl₄ and H₂O) on the native oxide covered (●) or the HCl-cleaned GaAs (○) are shown in Fig. 3. Panels (a) and (b) correspond to measurements under $V = +2$ V and negative biases of -1, -2, -3 V. The results for the samples with the thickest IL, i.e., grown from Hf[N(CH₃)₂]₄ and H₂O 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 ($h\nu < 3$ eV) modulated with another direct transition in GaAs [$\Lambda_3^v\text{--}\Lambda_1^c$ 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 ($\text{Hf}[\text{N}(\text{CH}_3)_2]_4 + \text{H}_2\text{O}$ 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 [panel (b)], suggesting IPE of holes from GaAs into HfO_2 . However, as compared to electron IPE [panel (a)], the character of yield variation is reversed: the yield is suppressed when exciting $\Gamma_8^v - \Gamma_7^c$ at $E_0' = 4.4$ eV but increases for the $X_7 - X_6 / \Sigma_v - \Sigma_c$ 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 HfO_2 bandgap edges:⁹ 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 $X_7 - X_6$ and $\Sigma_v - \Sigma_c$ excitations. The spectral threshold of hole IPE from the CB of GaAs into the VB of HfO_2 was evaluated from the $Y^{1/2} - h\nu$ plots shown in the inset in Fig. 3(b) to be close to $\Phi_h(\text{HfO}_2) = 3.8 \pm 0.2$ 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 HfO_2 with threshold $E_g(\text{HfO}_2) = 5.6$ eV, marked by arrows in Fig. 3.

Spectral thresholds of electron IPE were found using $Y^{1/3} - h\nu$ plots⁹ shown for the samples with thermal ALD Al_2O_3 and HfO_2 (HCl-cleaned sample) insulators in Figs. 4(a) and 4(b), respectively. The inferred IPE thresholds only weakly depend on the applied voltage, 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 Al_2O_3 (curves not shown) and HfO_2 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 Al_2O_3 of $\Phi_e(\text{Al}_2\text{O}_3) = 3.4 \pm 0.1$ eV, which corresponds to a CB offset of 2.0 eV. Samples with a HfO_2 insulator also exhibit nearly field-independent IPE threshold of $\Phi_e(\text{HfO}_2) = 3.3 \pm 0.1$ eV, yielding a comfortably large CB offset of 1.9 eV. The sample without HCl clean shows a lower threshold $\Phi_e(\text{IL}) = 2.3 \pm 0.1$ eV, which is close to the previously reported threshold for electron IPE from the GaAs VB into the CB of the Ga_2O_3 IL in $\text{GaAs}/\text{Ga}_2\text{O}_3/\text{GaGdO}_x$ structures⁷ as well as to the spectral threshold found for atomic-beam grown HfO_2 on GaAs.⁵

To conclude, we found both HfO_2 and Al_2O_3 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- κ 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,

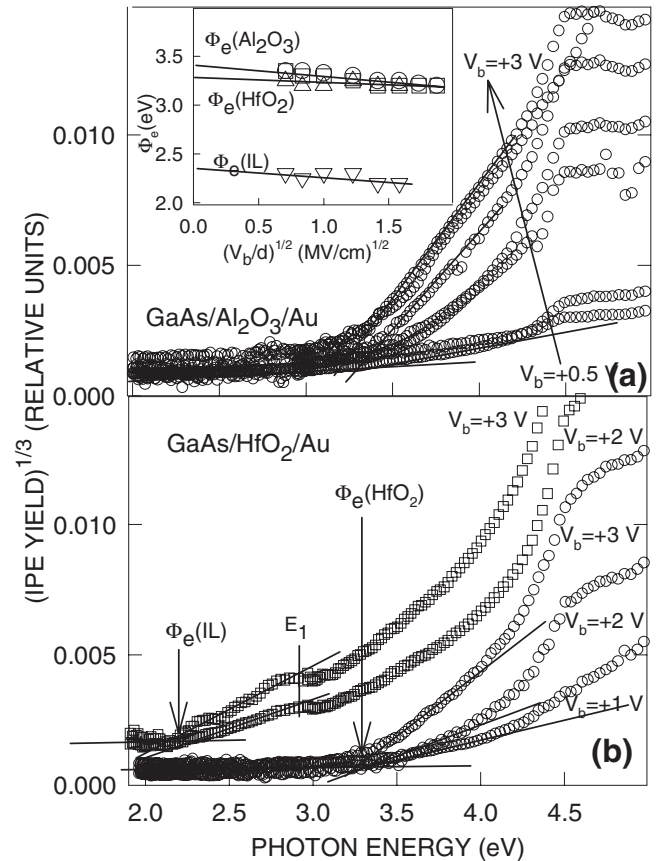


FIG. 4. Determination of the electron IPE spectral thresholds from $(\text{yield})^{1/3} - h\nu$ plots in samples with Al_2O_3 (a) and HfO_2 (b) insulators measured under different positive voltages applied to the Au top electrode. The inset in panel (a) shows the Schottky plot of the thresholds of electron IPE from the GaAs VB into the CB of Al_2O_3 (\circ , \square), HfO_2 (\triangle), and the IL (∇). Vertical arrows mark the observed threshold energies; lines guide the eye.

finding a way to remove the undesirable IL by a self-cleaning process.

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