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Band offsets of atomic-layer-deposited Al₂O₃ on GaAs and the effects of surface treatment

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The metal gate/high-*k* dielectric/III-V semiconductor band alignment is one of the most technologically important parameters. We report the band offsets of the Al/Al₂O₃/GaAs structure and the effect of GaAs surface treatment. The energy barrier at the Al₂O₃ and sulfur-passivated GaAs interface is found to be 3.0 ± 0.1 eV whereas for the unpassivated or NH₄OH-treated GaAs is 3.6 eV. At the Al/Al₂O₃ interface, all samples yield the same barrier height of 2.9 ± 0.2 eV. With a band gap of 6.4 ± 0.05 eV for Al₂O₃, the band alignments at both Al₂O₃ interfaces are established. © 2008 American Institute of Physics. [DOI: 10.1063/1.2976676]

The main difficulty that hinders the advancement of GaAs-based metal-oxide-semiconductor field-effect transistors is the low quality of gate dielectrics deposited on GaAs. Consequently, there have been many efforts to search for an electrically reliable and thermodynamically stable dielectric. In addition, the stringent requirement that the fabrication method of these dielectrics be compatible with Si-based device processing imposes a greater challenge. Several dielectrics have been investigated including Ga₂O₃(Gd₂O₃),¹ Al₂O₃,² and HfO₂.³ One of the deciding factors for the selection of an appropriate dielectric is the band offsets at the interfaces with the III-V substrate and the metal gate.⁴ Equally important are the physical and chemical interfacial properties that have a strong correlation with the GaAs surface conditions. For example, with a particular surface treatment of GaAs, the density of interfacial defect states can be reduced.⁵ In this letter, we report the band offsets of the Al/Al₂O₃/GaAs structure using internal photoemission (IPE) and spectroscopic ellipsometry (SE). As the GaAs substrate is subjected to different chemical treatments, the interface energy thresholds will be shown to change. Combined with both IPE and SE results, we establish the band offsets of the Al/Al₂O₃/GaAs structure and show that the barrier height is strongly affected by the initial conditions of GaAs.

Atomic layer deposition (ALD) was used to deposit four Al₂O₃ films on GaAs substrates that were subjected to three surface treatments: (i) unpassivated, (ii) NH₄OH, and (iii) S-passivated. Unpassivated GaAs was N₂ blown to remove surface particles. NH₄OH treatment was carried out by soaking the GaAs substrate in (NH₄OH) (29%) solution to remove the native oxide.⁵ The sulfur passivation was accomplished by dipping the sample in an HCl:H₂O=1:1 solution to remove the native oxide, then soaking in (NH₄)₂S at room temperature.⁶ Al₂O₃ thickness ranges from 10 to 12 nm. A 12 nm Al layer was evaporated on Al₂O₃ as a metal gate electrode.

IPE measurements and data analysis were performed on a system described elsewhere.⁷ The IPE quantum yield *Y* is calculated as the ratio of the photocurrent to the incident light flux. The band gap *E_g* is obtained from the Tauc-plot which is derived from ellipsometric data.⁸ Representative IPE square-root yield spectra in Fig. 1 for electron photoemissions from the Al electrode to the Al₂O₃ dielectric show the same energy threshold of 2.0 eV for both NH₄OH and S-passivated samples under an applied field of 1.5 MV/cm. The barrier heights at Al/Al₂O₃ interfaces for all samples were determined by applying biases from -2.0 to 2.0 V and are presented by Schottky plots in Fig. 2. Linear fits of the barrier heights to the square root of the electric field (*F*) result in a *zero-field* barrier height of $2.9 \text{ V} \pm 0.2 \text{ eV}$ from the Al Fermi level to the bottom conduction band of Al₂O₃, which is consistent with the barrier height of an Al/Al₂O₃ stack on a Si substrate.⁹ Although the reduction in the barrier height due to the oxide field strength appears to follow the classical image force model, it is rather stronger than

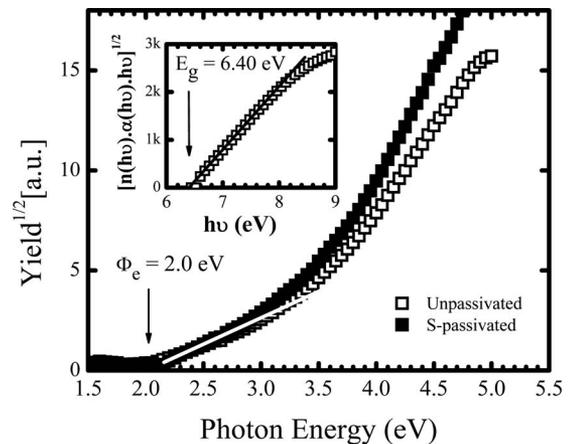


FIG. 1. Square root of the IPE yield from Al as a function of photon energy. Filled and open symbols are for S-passivated and unpassivated samples, respectively. The inset is the Tauc-plot for optical band gap determination where *n*, *α*, and *hν* are index of refraction, absorption coefficient, and photon energy, respectively.

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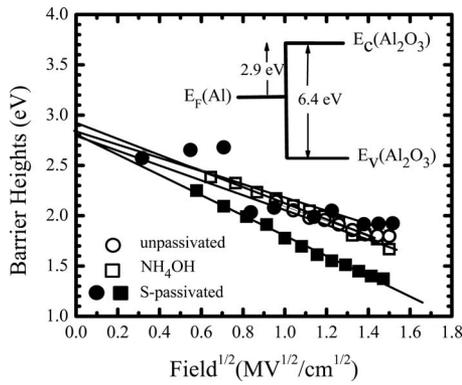


FIG. 2. Schottky plots of the spectral thresholds for photoemission from Al into Al₂O₃ conduction band. Filled circles and squares are for S-passivated, open circles are for unpassivated, and open squares are for NH₄OH-treated samples. The inset illustrations are the schematic band offsets at Al/Al₂O₃ interface.

expected.¹⁰ It is likely that local oxide charges distributed along the interface create additional field acting on the IPE carriers causing an additional reduction. How this added field distorts the image force barrier is a rather complex problem. A simplified model treating these local charges as a Coulomb potential in the oxide does show that the fixed charges can lead to reductions in the effective potential at the top of the barrier in the oxide.¹¹

The inset of Fig. 1 depicts a linear dependence near the absorption edge from which E_g is extracted to be 6.4 eV. The band gap of the amorphous Al₂O₃ thin film is lower than that of the well-ordered bulk Al₂O₃ and has been known to vary with the deposition or growth conditions. Such lowering has been associated with the defect-induced states existing in the band gap¹² and also been theoretically shown that it could be the result of Al atoms having lower coordination numbers than those of well-ordered Al₂O₃.¹³ Combining the zero-field barrier height ($\Phi_0=2.9$ eV) and the band gap yields a band offset of 3.5 ± 0.2 eV between the top of the valence band of Al₂O₃ and the Al Fermi level.

The energy threshold for electrons emitted from the top valence band of GaAs to the bottom conduction band of Al₂O₃ is found to be different for samples with the NH₄OH-treated/unpassivated and S-passivated GaAs. The barrier heights extracted from $Y^{1/3}$ for NH₄OH- and S-passivated samples are shown in Fig. 3 with an applied electric field of 1.12 MV/cm. It is obvious that the spectral threshold of the S-passivated sample shifts 0.6 eV lower than that of NH₄OH sample. Above the threshold, the yield of the S-passivated sample is reduced and plateaus at 2.92, 3.15, and 4.50 eV and dips at 4.98 eV. These features are bulk GaAs photon absorptions corresponding with the valence band spin-orbit splitting (E_1 and $E_1+\Delta_1$) and the higher interband critical points, E'_0 and E_2 , of GaAs.¹⁴ A slight increase in the yield slope at 3.4 eV appears to indicate a possible hole photoemission from the Al Fermi level to the top of the Al₂O₃ valence band because this energy coincides with the band offset between the Al Fermi level and the top valence band of Al₂O₃.

Higher IPE yield is observed in the S-passivated sample as seen in the inset of Fig. 3. It is due to the effects of passivation, which reduce the interfacial oxide, gap state densities, and recombination rates.¹⁵ It is known that As₂O₃ and Ga₂O₃ are formed when a clean GaAs surface is exposed

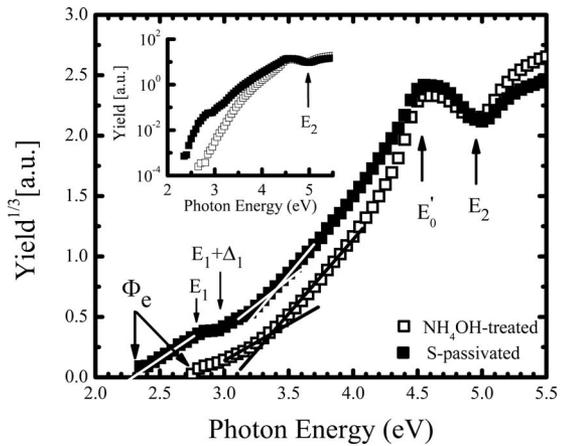


FIG. 3. Cube root of the IPE yield from GaAs as a function of photon energy. Filled and open symbols are for S-passivated and NH₄OH-treated samples, respectively. The inset shows the corresponding yields.

to air, leaving bare arsenic atoms embedded within the native oxide near the oxide/GaAs interface. It is also known that As₂O₃ is mobile at the grain boundaries and induces a non-uniform As₂O₃-rich layer. Such an interfacial layer causes an increase in the overall oxide thickness and carrier scatterings and reduces the escape probabilities of photoelectrons, therefore, leading to a reduction in oxide photocurrents. On the other hand, sulfur passivation creates gallium and arsenic atom bondings with sulfur atoms¹⁶ and significantly increases photon-excited electron conductivity.¹⁵

The field-dependence barrier heights for all samples were similarly extracted and are plotted in Fig. 4 in Schottky coordinates. The zero-field barrier heights (Φ_0) of 2.88 and 3.08 eV for the two S-passivated samples are both lower than those of unpassivated and NH₄OH-treated samples. A higher barrier height of 3.2 eV was also reported for a HF-treated GaAs via the Fowler–Nordheim tunneling method.¹⁷ With a 0.3 eV difference in the band gaps of Si and GaAs, the zero-field barrier height of 3.6 eV for unpassivated and NH₄OH-treated samples is interestingly consistent with the previously reported barrier height of 3.25 eV for the Al₂O₃/Si interface.⁹ An x-ray photoelectron spectroscopy (XPS) study also indicated a shift of 0.1 eV in binding en-

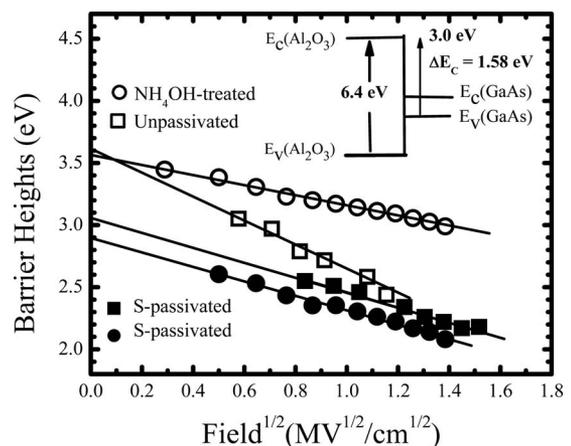


FIG. 4. Schottky plot of the energy barrier heights at Al₂O₃/GaAs interface. Filled circles and squares are for S-passivated, open circles are for unpassivated, and open squares for NH₄OH-treated samples. The inset illustrations are the schematic band offsets at Al₂O₃/GaAs interface.

ergy for a NH_4OH -treated GaAs surface relative to the $(\text{NH}_4)_2\text{S}$ -treated surface.¹⁸ Although the NH_4OH treatment may enhance the ALD growth mechanism by creating the OH group at the starting surface, charge transfer may create a dipole layer that modifies the barrier characteristics. The same is true for the case of the unpassivated surface of GaAs where a native oxide remains on the surface before ALD deposition. In all three surface treatments, the linear reduction in the barrier height as a function of the oxide field follows the image force model. However, the rather stronger linear field dependence (larger slope of the empty-square curve in Fig. 4 of the barrier heights for unpassivated GaAs) likely indicates a higher density of fixed charges in the oxide near the interface. A small threshold difference of 0.2 eV for the two S-passivated samples is likely due to a slight variation in the sulfur passivation chemistry and procedure performed at two laboratories and, as a result, is possibly indicative of the Fermi level unpinning by sulfur passivation. Nevertheless, the sulfur passivation has modified the interfacial electronic states yielding a 0.6 eV barrier height reduction compared with those of unpassivated and NH_4OH -treated GaAs. The role of sulfur passivation is to form the S-S, S-As, and S-Ga bonds at the surface.⁶ These bonds are chemically stable and are known to reduce the surface density states,¹⁹ thus changing the surface fixed charges and minimizing interface reaction, and as a result, changing the barrier height. A spectral threshold of 3.0 ± 0.1 eV, averaged from the two S-passivated samples is extracted as the zero-field barrier height from the top of the GaAs valence band to the bottom of the Al_2O_3 conduction band. Taking into account the 1.42 eV band gap of GaAs, the band offset diagram is drawn (see the inset of Fig. 4).

The IPE results presented above are in excellent agreement with the band offsets of $\text{Al}_2\text{O}_3/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ recently reported by Huang *et al.*²⁰ Their high resolution XPS (HR-XPS) data detect no residual arsenic oxides at the interface. From combined HR-XPS and *C-V* data, they determined the conduction band offset (ΔE_c) of 1.6 eV, the valence-band offset (ΔE_v) of 3.83 eV, and the electron affinity of 4.18 eV for $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$. With the GaAs electron affinity of 4.05 eV, ΔE_c is adjusted as if GaAs were a substrate and becomes 1.47 eV, which agrees with the IPE value of 1.58 eV within the experimental uncertainty (see Fig. 4).

In conclusion, we have employed IPE and ellipsometry to construct the band alignment of the $\text{Al}/\text{Al}_2\text{O}_3/\text{GaAs}$ structure. An energy height of 2.9 ± 0.2 eV was found for the $\text{Al}/\text{Al}_2\text{O}_3$ interface barrier. At the $\text{Al}_2\text{O}_3/\text{GaAs}$ interface, it is 3.0 ± 0.1 eV for sulfur-passivated GaAs and 3.6 eV for NH_4OH and unpassivated GaAs. The energy barrier height reduction is explained by the effect of sulfur passivation to eliminate the surface oxide of GaAs to reduce gap state densities and to lower recombination rates.

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