Band offsets of Al$_2$O$_3$/In$_x$Ga$_{1-x}$As ($x=0.53$ and $0.75$) and the effects of postdeposition annealing

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Band offsets at the interfaces of In$_x$Ga$_{1-x}$As/Al$_2$O$_3$/Al where $x=0.53$ and $0.75$ were determined by internal photoemission and spectroscopic ellipsometry. The photoemission energy threshold at the In$_x$Ga$_{1-x}$As/Al$_2$O$_3$ interface was found to be insensitive to the indium composition but shifted to a lower energy after a postdeposition annealing at high temperatures. Subthreshold electron photoemission was also observed for the annealed sample and was attributed to interfacial layer formation during the annealing process. © 2010 American Institute of Physics. [doi:10.1063/1.3306732]

High-mobility III-V compound semiconductor channel materials coupled with a high-$\kappa$ gate dielectric have recently become a major focus as a possible technology to support the further scaling of the advanced complimentary metal-oxide-semiconductor (MOS) field-effect transistors technology. While significant progress has been made recently, many challenges remain. One of the main challenges is the formation of a high quality gate dielectric-substrate interface. Many high-$\kappa$ oxides have been investigated throughout the years including molecular-beam epitaxial Ga$_2$O$_3$/Gd$_2$O$_3$ mixture, atomic layer deposited (ALD) Al$_2$O$_3$, HfO$_2$, and Al$_2$O$_3$-aSi.$^7$ The existing consensus is that the native oxide on the III-V compound substrate must be avoided prior to the deposition/growth of the gate oxides. Also at least the oxides must also have band offsets larger than 1 eV to prevent unacceptably large leakage current.$^8$ In this letter, combining internal photoemission (IPE) with spectroscopic ellipsometry (SE), we investigated the energy barrier and band offsets at interfaces of ALD Al$_2$O$_3$ on In$_{0.53}$Ga$_{0.47}$As and In$_{0.75}$Ga$_{0.25}$As substrates. The interest in higher indium content composition is due mainly to the higher achievable drive current.$^8$ The smaller band gap of the high indium content InGaAs substrate also moves the contact Fermi level closer to the contact metal conduction band leading to a more ideal ohmic contact.$^9$ The energy barrier height from the top valence band of the InGaAs to the bottom conduction band of Al$_2$O$_3$ is found to be essentially the same for both indium concentrations. We also observed a barrier energy lowering phenomenon due to high temperature annealing. It appears that annealing induces the formation of an interfacial layer between the substrate and the oxide.

In this study, MOS structures consisting of Al gate, Al$_2$O$_3$ insulator, and both p+ and n+ doped In$_{0.53}$Ga$_{0.47}$As and In$_{0.75}$Ga$_{0.25}$As were used.$^{11}$ An 8 nm Al$_2$O$_3$ layer was grown by atomic-layer deposition after removing the native surface oxide by a buffered-oxide-etch solution and soaking in ammonium sulfide for 10 min. Postdeposition annealing (PDA) in N$_2$ gas was performed at 650 and 600 °C for 30 s. A 12 nm thick Al layer was then thermally evaporated on top of Al$_2$O$_3$. IPE measurements were performed with the bias applied to the substrate from $-2$ to 2.0 V in steps of 0.1 V, and the photoemission yield is calculated as the ratio of the measured photocurrent to the incident light flux. The electric field in the Al$_2$O$_3$ layer was the applied voltage minus the built-in potential which was estimated at the applied voltage when the photocurrent switched direction (see Fig. 1). The dielectric functions of In$_{0.53}$Ga$_{0.47}$As, In$_{0.75}$Ga$_{0.25}$As and Al$_2$O$_3$, and the Al$_2$O$_3$ band gap were determined by SE.

The pseudodielectric function of Al$_2$O$_3$ is found to be essentially the same for all samples. In Fig. 1 the Al$_2$O$_3$ optical band gap of 6.8 eV was determined from the Tauc plot.$^{12}$ Figure 2(a) shows the imaginary part ($\varepsilon_2$) of the pseudodielectric functions of In$_{0.75}$Ga$_{0.25}$As and In$_{0.53}$Ga$_{0.47}$As with the three critical points $E_1$, $E_1 + \Delta_1$, and $E_2$.

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** (Color) Typical photocurrents of PDA Al$_2$O$_3$/In$_{0.75}$Ga$_{0.25}$As sample with the substrate biased from $-2$ to 0 V to demonstrate how the oxide built-in potential is determined. The current switches direction at about $-0.55$ V, which is the built-in voltage. The Al$_2$O$_3$ band gap is extracted from the Tauc-plot (right axis) by linear fitting of $[n(E)\alpha(E)]^{1/2}$ where $n(E)$ is the index of refraction and $\alpha(E)$ the absorption coefficient.

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E2 which are shifted to lower energy for higher indium concentration.13 Reductions in the photocurrent are seen between 2.4 and 2.8 eV and between 4.5 and 4.8 eV [Fig. 2(b)]. The reduction at E2 is due to the strong absorption or the decreasing light penetration depth and the Xc critical point final state of the E2 transition in the X crystal momentum direction being well below the Al2O3 bottom conduction band.14

A series of Y1/3-hv plots, shown in Fig. 2(b), measured at a substrate bias of −2.0 V for all samples, clearly indicate that PDA samples have a lower energy threshold than those of as-deposited samples. The spectral thresholds (Φe,s) extracted by linear fits correspond to IPE from the InGaAs valence band maximum to the Al2O3 conduction band minimum. A 0.3 eV redshift is observed for all annealed samples with respect to the as-deposited samples. A similar redshift was reported when GaAs surface was treated,15 leading us to speculate that, the shift may be caused by the interfacial chemical modification. It also is interesting to note that when Al2O3 is annealed at much higher temperature (>800 °C), a blueshift was observed and attributed to the Al2O3 phase change.16

Another significant observation is the subthreshold IPE signals as indicated by Φint in Fig. 2(b), possibly due to the formation of an interlayer between the substrate and Al2O3. Similar subthreshold photoemission has been shown to originate from an intentionally grown interlayer between the III-V substrates and the Al2O3 and HfO2 gates.17 While we have no direct evidence, this layer is likely to be a mixture of oxides or suboxides containing Ga, As, and In where In oxides do not seem to play a significant role to the band offset as discussed below. Furthermore, the high temperature PDA induced a thicker interfacial layer with a higher state density as evidenced by a stronger emission below the principal threshold (Φc). For the as-deposited samples, a weaker sub-threshold signal [see Fig. 2(b)] is indicative of a thinner interfacial layer. The same conclusion is suggested by the relatively weaker E1 and E1 + Δ1 features in the IPE signal.

The spectral thresholds (Φe) were determined by fitting the conventional Fowler plots Y1/2-hv as shown in Fig. 3. The subthreshold tails are believed to relate to the conduction band tail states of Al2O3 and/or the lateral nonuniformity of the barrier.18 Schottky plots depicted in the inset of Fig. 3 display a rather weak field dependence of the Al/Al2O3 barrier heights for all samples as indicated by three different values in the inset figure. The barrier height variation does not have a consistent relation with the treatment condition of Al2O3. Since the Al2O3 surface was exposed to air ambient for a long period of time prior to Al deposition, it is quite probable that the contamination may contribute to the variation, as it is well known that the Al/Al2O3 electronic interface properties are strongly dependent on growth and surface conditions. In fact, metal/high-κ oxide interface barriers have been shown a strong sensitivity to the interface chemical nature.19 It is also noticed that, since the IPE quantum yields are much weaker for the large barrier height samples, it is indicative of lower interfacial transition probabilities of photocarriers accumulated at the larger barrier height interface. Furthermore, external field dependence of the barrier height is almost constant; i.e., very insensitive to the applied external electric field. In contrast to the metal/SiO2 systems where the image-force interaction is significant, it has been documented that such interaction is much reduced in the metal/high-κ system. It has been suggested that the cause of barrier height insensitivity is likely due to the existence of a plane of negative charges distributed in the high-κ close to the metal.18

Figure 4 displays a series of Schottky plots characterizing the Al2O3 electric field dependence of the barrier heights (Φc) at the Al2O3/InGaAs interface for all samples. Within 0.1 eV uncertainties, the zero-field barrier heights (Φc) of as-deposit and PDA Al2O3 on In0.53Ga0.47As and...
In$_{0.75}$Ga$_{0.25}$As substrates can be reasonably averaged to a value of 3.30 and 2.95 eV, respectively. Therefore it is concluded that the effect of PDA is to reduce the barrier height of 0.35 eV which is also clearly seen as a redshift in Fig. 1. The barrier height value from as-deposited Al$_2$O$_3$ is in good agreement with the reports of the IPE study on unannealed ALD Al$_2$O$_3$ on In$_{1-x}$Ga$_x$As where the indium varied from 0% to 53%. It is also illuminating to compare our results with the recent X-ray photoelectron spectroscopy and reflection electron energy loss spectroscopy study, where the authors showed that the barrier height of 600 °C annealed ALD on In$_{1-x}$Ga$_x$As (x <0.5) varied from 2.84 to 3.11 eV, which is consistent with the lower barrier height obtained from PDA samples in this study. It is important to note that within the measurement uncertainty the barrier height does not change with respect to the large indium concentration difference. This means that the top of the valence band pins at the same energy position with respect to the bottom Al$_2$O$_3$ conduction band. The same conclusion was reached by a similar study but with the lower indium concentration (<50%) in the InGaAs (Ref. 20) and theoretically predicted where they show a much larger offset of the conduction band than that of valence band for GaAs and InAs.

From the band gaps of In$_{0.53}$Ga$_{0.47}$As and In$_{0.75}$Ga$_{0.25}$As being 0.75 and 0.55 eV, respectively, we conclude that the conduction band offset is 2.55 and 2.75 eV for as deposited Al$_2$O$_3$ on In$_{0.53}$Ga$_{0.47}$As and In$_{0.75}$Ga$_{0.25}$As, respectively, and 2.20 and 2.40 eV for PDA Al$_2$O$_3$ on In$_{0.53}$Ga$_{0.47}$As and In$_{0.75}$Ga$_{0.25}$As, respectively. However, the valence band offset is essentially the same for both substrates since the barrier heights were found insensitive to the indium content. Therefore, from the Al$_2$O$_3$ band gap of 6.80 eV measured by SE, the valence band offset becomes 3.85 and 3.50 eV for PDA and as-deposited Al$_2$O$_3$, respectively. Figure 4 also displays that the zero-field barrier height of the interlayer was averaged to a value of 2.2 ± 0.3 eV. The annealing effect and the existence of the interlayer appear to degrade the current-voltage characteristics as we find that ALD Al$_2$O$_3$ have higher leakage currents than that of as-deposited samples (not shown). Finally, with the conduction band offset much larger than 1.0 eV, ALD Al$_2$O$_3$ should be suitable to use in a high mobility MOS device as long as the formation of the interlayer of lower barriers can be avoided, and the substrate surface chemistry must be well controlled to achieve stable and reliable devices.

In summary, using internal photoemission and SE we study the band offsets of atomic-layer-deposited Al$_2$O$_3$ on two different indium concentration substrates, In$_{0.53}$Ga$_{0.47}$As and In$_{0.75}$Ga$_{0.25}$As, and subjected then to postdeposition annealing. The barrier height is found to be insensitive to the indium amount. When comparing as-deposited and post-deposition annealed Al$_2$O$_3$, we find a redshift to 0.3 eV of the barrier height when Al$_2$O$_3$ is annealed at high temperature. In addition, a spectral threshold was clearly observed in annealed Al$_2$O$_3$, implying the formation of an interlayer of possible different chemical nature under thermal annealing.

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