Band alignment between (100) Si and amorphous $LaAlO_3$, $LaScO_3$, and Sc_2O_3: Atomically abrupt versus interlayer-containing interfaces

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Incorporation of a ~1-nm-thick SiO_x interlayer is found to have little effect on the band alignment between a (100) Si substrate and amorphous $LaAlO_3$, $LaScO_2$, and Sc_2O_3 insulators. All of these materials are found to give the same band offsets irrespective of differences in their composition, even when contacting Si directly. This suggests that the bulk electron states and properties of the semiconductor and insulator layer play a much more important role in determining the band lineup at the interface than any dipoles related to particular bonding configurations encountered in the transition region between Si and these oxides. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2164432]

The impact of atomic bonding on the spectrum of electron states at semiconductor/insulator interfaces is of significant interest in the search for candidate gate insulator materials for metal-oxide-semiconductor (MOS) devices. Generally, the interface band alignment is believed to be determined by two major contributions:[1] The intrinsic contribution related to *bulk* electronic properties of the contacting solids and an *interface component* determined by specific atom bonding configurations. Experiments indicate that the conduction band (CB) offset between (100) Si and a number of dissimilar metal oxides (ZrO_2, HfO_2, Lu_2O_3, $LaAlO_3$, $LaScO_3$, $GdScO_3$, and $DyScO_3$) is nearly the same (≈2 eV, Refs. 2–4), suggesting the interface contribution to the barrier to be insignificant. However, one might argue that the results are still affected by a Si oxide interlayer (IL), should it result in the same dipole for all the studied metal oxides. The obvious task then is to compare the band offsets at atomically abrupt Si/insulator interfaces to those measured in the presence of an IL. Here we report on measurements of the band alignment at SiO_x-free (<0.02 nm) interfaces of (100) Si with several amorphous insulators ($LaAlO_3$, $LaScO_3$, and Sc_2O_3) grown by the molecular beam deposition (MBD) technique[5] as compared to the $LaAlO_3$ and $LaScO_3$ layers grown on ≈1-nm-thick SiO_x using pulsed laser deposition (PLD).[6] As the observed band alignments appear to be the same, the band offsets are hypothesized to be determined by the intrinsic electronic properties of the semiconductor and by the projection of the density of states (DOS) of the insulator into the band gap of the nanometer-thin IL.

The studied samples were prepared by two different deposition methods: MBD and PLD. The MBD growths on hydrogen-terminated (100) Si surfaces were carried out at temperatures <100 °C.[5,7] Importantly, the previous physical analysis of the samples indicated that, even after transfer in the room ambient, they have less than 0.02 nm (less than 0.1 ML) of Si oxide at the interface, i.e., the metal oxide is in *direct contact* with Si at least on 90% of the interface area.[5] Some of the samples received an additional 10 min anneal at 650 or 800°C in N_2+5% O_2 to remove H from the interface and allow atomic interactions between Si, the oxide, and the supplied oxygen.[7] In contrast, the PLD oxides were grown on chemically oxidized (100) Si resulting in a ~1-nm-thick silicon oxide IL (Fig. 1 in Ref. 6). The amorphous metal oxide layers produced by both methods were 20–40 nm thick. MOS capacitors were fabricated by evaporation of 15-nm-thick Au or Al electrodes. The interface band diagram and the oxide band gap were determined using internal photoemission (IPE) and photoconductivity (PC) measurements in the spectral range $2<h\nu<6.5$ eV.[2]

The major results are summarized in Figs. 1 and 2 showing the IPE/PC quantum yield as a function of photon energy $h\nu$ in MOS capacitors with $LaAlO_3$ and $LaScO_3$ insulators, respectively, grown by both PLD (circles) and MBD (squares). The open/closed symbols correspond to the data taken with positive/negative bias on the Au electrode. The spectral thresholds of electron transitions corresponding to IPE from Si and to PC of the oxide [cf. definitions in the inset in Fig. 1(a)] were determined from the $(\text{yield})^{1/3}-h\nu$ and the $(\text{yield})^{1/2}-h\nu$ plots, respectively. These plots were linearly extrapolated to zero yield after subtracting photocurrent(s) with lower threshold(s). The threshold photon energies determined in this way lie close to the intersection of the straight lines as shown in Figs. 1(b) and 2(b). Both $LaAlO_3$ and $LaScO_3$ grown by MBD exhibit a PC threshold at 5.7±0.1 eV, corresponding to the lowest oxide band gap E_g, which is the same as for the PLD samples.[4] In addition, there is a subthreshold PC with apparent onset at $E_g^* \approx 4.5$ eV [cf. panels (b) in Figs. 1 and 2]. The IPE of electrons from the Si valence band (VB) is observed under positive metal bias (○, □) and has a threshold at 3.0–3.1 eV with a weak sensitivity to the strength of the applied electric field which is consistent with a high dielectric constant of the studied oxides. Extrapolation to zero field using the Schottky plot (not shown) gives the barrier height (between the VB of Si and the CB of

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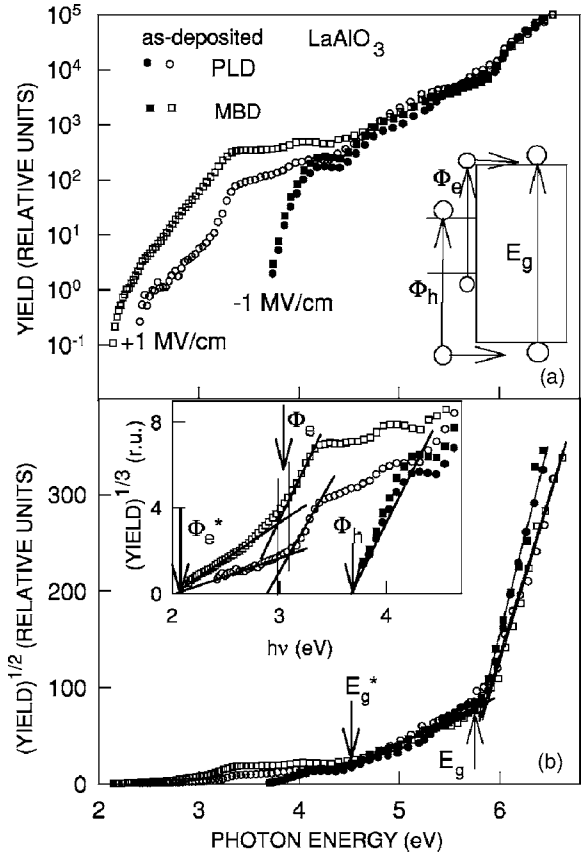

FIG. 1. (a) IPE/PC yield as a function of photon energy measured in MOS capacitors with ≈20-nm-thick layers of amorphous $LaAlO_3$ deposited by PLD on (100) Si covered with a ~1-nm-thick chemical oxide (circles) or by MBD directly on the (100) Si surface (squares). The open/closed symbols correspond to data taken with positive/negative bias on the Au electrode, respectively, with an average electric field strength in the oxide of 1 MV/cm. The insert in panel (a) diagramatically shows the observed electron transitions and the corresponding energy thresholds. Panel (b) and the inset illustrate the determination of the spectral thresholds.

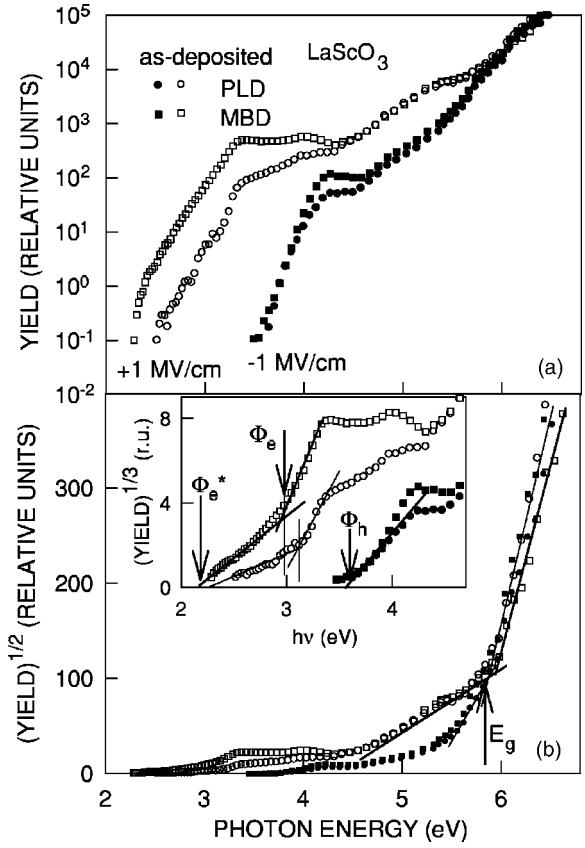

FIG. 2. (a) IPE/PC yield as a function of photon energy measured in MOS capacitors with ≈20-nm-thick layers of amorphous $LaScO_3$ deposited by PLD on (100) Si covered with a ~1-nm-thick chemical oxide (circles) or by MBD directly on the (100) Si surface (squares). The open/closed symbols correspond to the data taken with positive/negative bias on the Au electrode with an average electric field strength in the oxide of 1 MV/cm. Panel (b) and the inset illustrate the determination of the spectral thresholds.

the oxide) $\Phi_e = 3.1 \pm 0.1$ eV for both MBD and PLD layers [with an accuracy of ±0.1 eV, cf. insets in panels (b) in Figs. 1 and 2], corresponding to a CB offset of 2.0±0.1 eV. The major difference between the MBD and PLD samples consists in a much reduced quantum yield of IPE in the presence of a 1-nm-thick SiO_x in the PLD case indicating additional scattering of the photoexcited electrons within the IL.[8] In addition, the electron IPE exhibits a significant subthreshold portion with an apparent threshold $\Phi_e^* \sim 1$ eV below the main IPE threshold, indicating oxide CB tailing as the main reason for the observed subthreshold PC.

Similar trends are observed in the spectra measured when the metal is biased negatively (●, ■). The same spectral threshold $\Phi_h = 3.7 \pm 0.1$ eV is found for both kinds of deposited oxides, but the yield is reduced in the presence of the SiO_x. The latter, together with the observation of the same threshold in the Al- and Au-gates samples, indicates that the hole IPE from the CB of Si into the oxide VB dominates the photocurrent. Indeed, the oxide band gap calculated from the barrier values, $E_g = \Phi_e + \Phi_h - E_g(\mathrm{Si}) = 5.7$ eV, appears to be well in agreement with the PC results. As no subthreshold IPE of holes is observed, the density of the tail states above the oxide VB is concluded to be insignificant.

The close similarity between spectra obtained from MOS capacitors with $LaAlO_3$ (Fig. 1) and $LaScO_3$ (Fig. 2) insulators indicates that the change of Al to Sc has little effect on the band gap and band offsets of these amorphous complex oxides. Interestingly, the band gap of amorphous Sc_2O_3 is only about 4 eV,[9] as compared to 6–6.2 eV for amorphous alumina.[2] A large band gap difference is also observed for the crystalline phases: 6–6.3 eV for Sc_2O_3 (Refs. 10 and 11) and 8.7 eV (Ref. 1) for sapphire.[12,13] The absence of such a difference between amorphous $LaAlO_3$ and $LaScO_3$ indicates that the CB edge energy position is mostly determined by the 5*d* states of La, while unoccupied 3*d* states of Sc, which constitute the bottom of the Sc_2O_3 CB,[14] are likely to lie at a higher energy. To verify this supposition we analyzed the IPE/PC spectra of Sc_2O_3 layers deposited by MBD presented in Fig. 3. The as-deposited amorphous Sc_2O_3 exhibits a gap of 5.6 eV, as determined from the PC portion of the spectra shown in Fig. 3, which is considerably higher than that inferred for the sputtered films in Ref. 9. From the IPE spectra for the Si/Sc_2O_3 interface the barrier heights for electrons and holes were found to be nearly the same as for the complex La oxides: $\Phi_e = 3.0 \pm 0.1$ and $\Phi_h = 3.7 \pm 0.1$ eV. Upon annealing at 650°C the gap of Sc_2O_3 increases to 6.0±0.1 eV, while the barrier height for electrons remains the same (spectra not shown) suggesting a ≈0.4 eV downshift of the oxide VB top. This effect may be related to crystallization of scandia for which a band gap of 6.0-6.3 eV was reported.[10,11]

Another way of introducing an IL between Si and the metal oxide is postdeposition oxidation of the sample. Indeed, as can be seen from the comparison of the results for

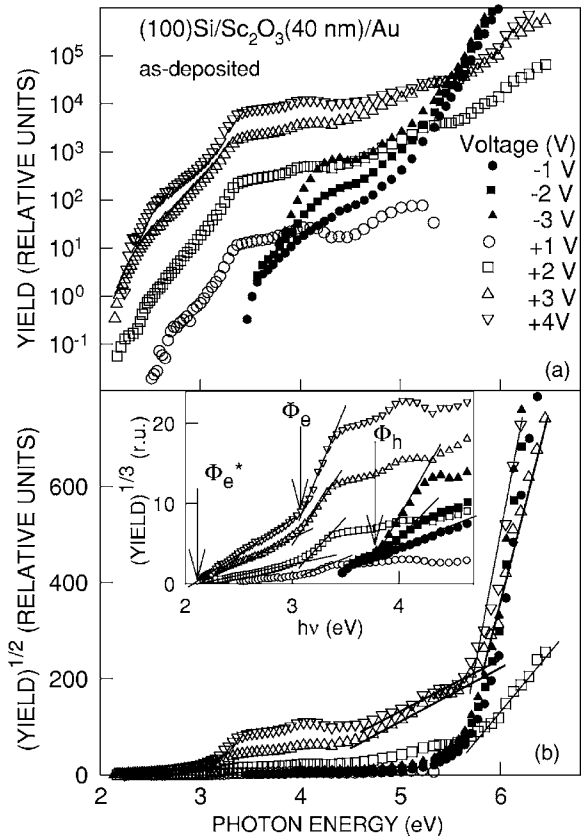

FIG. 3. (a) IPE/PC yield as a function of photon energy measured in MOS capacitors with a 40-nm-thick layer of amorphous Sc_2O_3 grown by MBD directly on (100) Si. The open/closed symbols correspond to data taken with the indicated positive/negative bias on the Au electrode. Panel (b) and the inset illustrate the determination of the spectral thresholds.

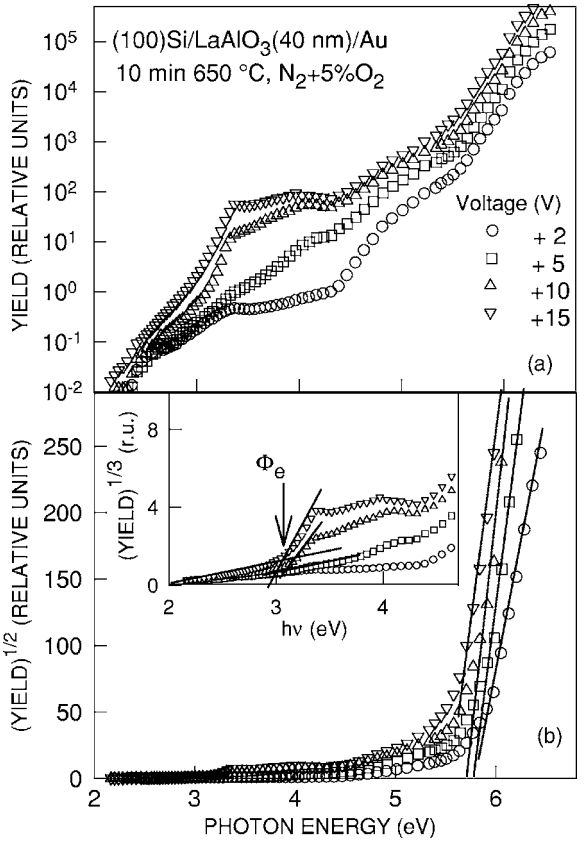

FIG. 4. (a) IPE/PC yield as a function of photon energy measured for different values of positive gate bias in MOS capacitors with a 40-nm-thick layer of amorphous $LaAlO_3$ grown by MBD and subsequently oxidized for 10 min in $N_2+5\%$ O_2 at 650 °C and 1 atm. Panel (b) and the inset illustrate the determination of the spectral thresholds from the yield power plots.

the as-deposited and 650°C oxidized MBD $LaAlO_3$ samples (□ in Figs. 1 and 4, respectively), the IPE yield from Si measured at the same field significantly decreases, indicating the growth of a SiO_x interlayer. The IL thickness of (evaluated from the decrease in accumulation capacitance of the MOS structure) is about 1.5–2 nm which is consistent with the stronger impact of this IL on the electron IPE as compared to the case of a ~1-nm-thick chemical SiO_x [cf. ○ in Figs. 1(a) and 4(a)]. However, as the strength of electric field increases, the IPE into the CB of $LaAlO_3$ is seen to occur without any measurable shift in the IPE spectral threshold [compare △,▽ in the inset in Fig. 4(b) to □ in the inset in Fig. 1(b)]. Besides affirming that the IL has little effect on the band lineup at the interface, this result indicates another important feature. Naïve thinking would lead one to expect a downshift in energy of the metal oxide CB DOS caused by the potential drop across the IL. The absence of this effect shows that the CB DOS of $LaAlO_3$ is present, albeit strongly attenuated, in the SiO_x band gap, probably, due to quantum penetration of the aluminate band states into the IL. Therefore, it appears that the band lineup at the studied interfaces is essentially determined by the bulk DOS of the semiconductor and insulator(s). A tentative explanation of this behavior consists in a dominant (as compared to the IL) contribution of bulk electron states of the semiconductor to the electron density projected into the oxide band gap. The density of these "tail states" will be basically governed by their density and energy in the Si crystal, and by the band gap width of the insulator. As a result, for the same semiconductor, oxides with close band gap width and dielectric constant will yield similar band offset values.

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