Measurement of the band offsets between amorphous LaAlO₃ and silicon

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The conduction and valence band offsets between amorphous LaAlO₃ and silicon have been determined from x-ray photoelectron spectroscopy measurements. These films, which are free of interfacial SiO₂, were made by molecular-beam deposition. The band line-up is type I with measured band offsets of 1.8 ± 0.2 eV for electrons and 3.2 ± 0.1 eV for holes. The band offsets are independent of the doping concentration in the silicon substrate as well as the amorphous LaAlO₃ film thickness. These amorphous LaAlO₃ films have a bandgap of 6.2 ± 0.1 eV. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1644055]

There is currently an extensive research effort to find alternative gate dielectrics to replace SiO₂ in metal-oxide-semiconductor field-effect transistors (MOSFETs) as SiO₂ approaches its fundamental limits. LaAlO₃ is a promising alternative gate dielectric for the replacement of SiO₂ in silicon MOSFETs.[1–3] Single-crystalline LaAlO₃ has a dielectric constant of 24.1 ± 0.2 measured at 145 GHz (Ref. 4) and has an optical bandgap of 5.6 eV.[5] Amorphous LaAlO₃ thin films on silicon have an estimated dielectric constant of 20–27.[6–8] It has also been shown that single-crystalline LaAlO₃ is stable in contact with silicon under standard MOSFET processing conditions of 1026 °C for 20 s.[9] The band offsets between LaAlO₃ and silicon have been predicted to be in the range of 1.0 to 2.1 eV for electrons and 1.9 to 3.5 eV for holes.[10,11] All of these properties meet the requirements for an alternative gate dielectric as suggested by the *International Technology Roadmap for Semiconductors* (ITRS).[12]

Although LaAlO₃/Si shows many promising properties, there are no published papers that have experimentally determined the band offsets. It is critical that the high-*K* gate dielectric have conduction band offsets (CBOs) and valence band offsets (VBOs) of at least 1 eV for both electrons and holes from the silicon.[12] In this letter, we report an experimental determination of the bandgap, CBOs, and VBOs of amorphous LaAlO₃ on silicon.

Amorphous LaAlO₃ thin films with the following thicknesses:[13] 10, 20, 40, and 150 Å were grown by molecular-beam deposition in an EPI 930 molecular-beam epitaxy chamber modified for the growth of oxides,[14] and shipped to Pacific Northwest National Laboratory (PNNL) for the x-ray photoelectron spectroscopy (XPS) measurements. The films were grown on *n*- and *p*-type Si (001) wa-

fers. The native SiO₂ on the silicon wafer was thermally removed in UHV at a temperature of 900 °C, measured with an optical pyrometer. The films were grown using elemental sources. Lanthanum, aluminum, and molecular oxygen (99.994% purity) at a background pressure of 6×10^{-8} Torr were codeposited at a thermocouple temperature of ~100 °C onto the clean 2×1 Si surface. The lanthanum and aluminum fluxes were each 2×10^{13} atoms/cm² s. Several 1000-Å-thick amorphous LaAlO₃ films have been analyzed by Rutherford backscattering spectrometry (RBS) (1.4 MeV He+, 170° scattering angle). It indicated that the films are stoichiometric, with a ratio of La:Al=1 ± 0.05. A 3000-Å-thick amorphous LaAlO₃ film on silicon was used to determine the bandgap of amorphous LaAlO₃ using a far-UV spectroscopic ellipsometer.[5]

Once the films were at PNNL in UHV, the O 1*s* core-level spectra indicated the presence of hydroxyls (OH) on the films. Polar-angle-dependent XPS measurements on a 150 Å LaAlO₃/Si film confirmed that the OH layer was only on the surface of the films and was not distributed within the entire film or at the LaAlO₃/Si interfacial region. Nuclear reaction analysis (NRA) was used to corroborate the presence of hydrogen. A series of *in situ* annealing steps were completed using NRA. NRA indicated that the hydrogen content was completely removed by a 10 min anneal at 400 °C in UHV. Figure 1 shows the O 1*s* core-level spectra before and after annealing. Such an annealing step was completed in the XPS chamber for all of the films measured in this letter. High-resolution scans of the Si 2*s* region were completed on the as-grown films and after annealing. The as-grown films, even as thin as 10 Å LaAlO₃/Si and exposed to air, were free of detectable SiO₂ at the interface.[15] After annealing at 400 °C in UHV, the XPS spectra contained a small peak at ~153 eV, indicating the formation of Si–O bonding.

A core-level photoemission-based method similar to that

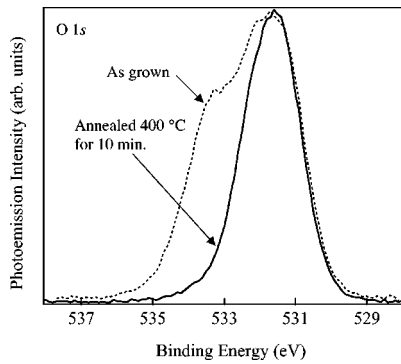[a)]Electronic mail: schlom@ems.psu.edu
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FIG. 1. High-energy-resolution O 1*s* core-level spectra for a 40-Å-thick amorphous LaAlO$_3$ film on *p*-Si(001) before and after annealing at 400 °C for 10 min in UHV.

of Kraut *et al.*[16,17] was used to determine the VBOs.[18] Appropriate shallow core-level peaks were referenced to the top of the VB for bulk Si(001) and a thick (150 Å) film of LaAlO$_3$ on Si(001), using a linear extrapolation method to determine the valence band maximum (VBM).[18–20] The resulting binding energy differences between the core peaks and VBMs for the pure materials were then combined with core-level binding energy differences for heterojunctions to obtain the VBO as a function of thickness and doping type. Monochromatic Al $K\alpha$ x rays at normal incidence with a GammaData SES 200 analyzer were used for all measurements. The XPS spectrometer was calibrated using a polycrystalline Au foil. The Au $f_{7/2}$ peak position and Fermi-edge inflection point were determined to be 84.00 ± 0.02 and 0.00 ± 0.02 eV, respectively. Therefore, all of the binding energies (BE) are accurate on an absolute scale within 0.02–0.03 eV, over the binding energy range of 0 to 100 eV.

A thick (150 Å) LaAlO$_3$/Si film was used to obtain the XPS spectra for bulk amorphous LaAlO$_3$. The 10, 20, and 40 Å LaAlO$_3$/Si films were thin enough to obtain XPS spectra from both the LaAlO$_3$ film and the underlying silicon.

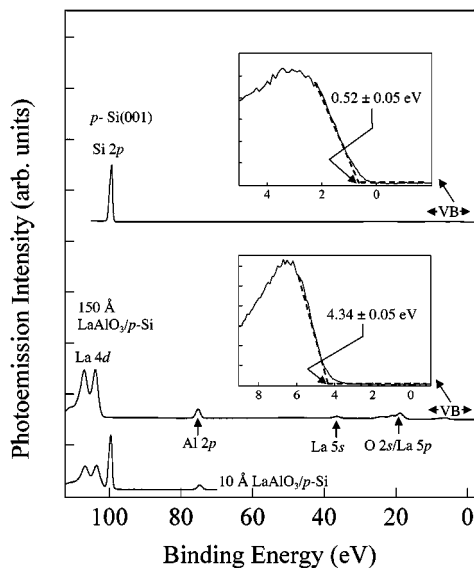Figure 2 shows the shallow core-level and VB spectra

FIG. 2. Shallow core-level and VB photoelectron spectra for bare *p*-Si(001) and 150 Å and 10 Å LaAlO$_3$/Si heterojunctions. The insets show high-resolution scans of the VB regions for the *p*-Si(001) and the 150 Å LaAlO$_3$/Si.

TABLE I. Summary of CBOs (ΔE_c) and VBOs (ΔE_ν) for a series of different thickness amorphous LaAlO$_3$ films on *n*- and *p*-type silicon.

Film	ΔE_c (eV)	ΔE_ν (eV)
10 Å LaAlO$_3$/*n*-Si	1.75 ± 0.2	3.35 ± 0.1
10 Å LaAlO$_3$/*p*-Si	1.93 ± 0.2	3.17 ± 0.1
20 Å LaAlO$_3$/*p*-Si	1.99 ± 0.2	3.11 ± 0.1
40 Å LaAlO$_3$/*n*-Si	1.76 ± 0.2	3.34 ± 0.1
40 Å LaAlO$_3$/*p*-Si	1.88 ± 0.2	3.22 ± 0.1

for bulk Si(001), a thick (150 Å) LaAlO$_3$/Si, and one of the 10 Å LaAlO$_3$/Si heterojunctions that was used to determine the band offsets. The VB value (E_ν) was determined by linearly fitting the leading edge of the VB and linearly fitting the flat energy distribution and finding the intersection of these two lines, as shown in Fig. 2 for silicon and the thick LaAlO$_3$/Si film. The energy differences between the VB edges and the Si 2*p* centroids $(E_{\text{Si }2p} - E_\nu)_{\text{Si}}$ were measured to be 98.90 ± 0.05 and 98.98 ± 0.05 eV for *n*- and *p*-type silicon wafers, respectively.[19,20] These results are in good agreement with the value of 98.95 ± 0.04 eV for *n*-type silicon measured by Yu *et al.*[21] For the thick (150 Å) LaAlO$_3$/Si, the leading edge of the VB relative to the Fermi level (FL) and the energy difference between the Al 2*p* centroid and the leading edge of the VB $(E_{\text{Al }2p} - E_\nu)_{\text{Thick LaAlO}_3}$, were measured to be 4.34 ± 0.05 and 70.86 ± 0.05 eV, respectively. The energy difference between the Si 2*p* centroid and the Al 2*p* centroid $(E_{\text{Si }2p} - E_{\text{Al }2p})_{\text{LaAlO}_3/\text{Si}}$ was determined for each of the LaAlO$_3$/Si heterojunctions. These values were then inserted into the following equations to calculate the VBOs (ΔE_ν) and CBOs (ΔE_c):

$$\Delta E_\nu = (E_{\text{Si }2p} - E_\nu)_{\text{Si}} - (E_{\text{Al }2p} - E_\nu)_{\text{Thick LaAlO}_3}$$
$$- (E_{\text{Si }2p} - E_{\text{Al }2p})_{\text{LaAlO}_3/\text{Si}} \qquad (1)$$

and

$$\Delta E_c = E_{g(\text{LaAlO}_3)} - E_{g(\text{Si})} - \Delta E_\nu, \qquad (2)$$

where $E_{g(\text{LaAlO}_3)}$ is the bandgap of amorphous LaAlO$_3$ and $E_{g(\text{Si})}$ is the bandgap of silicon. The VBOs and CBOs were determined for a series of films on *n*- and *p*-type silicon. Table I shows a summary of the band offset results. Both the CBO and VBO are independent of silicon doping as well as the thickness of the amorphous-LaAlO$_3$ film.

A 3000-Å-thick film of amorphous LaAlO$_3$ was grown on a silicon substrate to determine the bandgap of amorphous LaAlO$_3$ on silicon $[E_{g(\text{LaAlO}_3)}]$. The sample was measured in a spectroscopic ellipsometer system described previously.[5] The initial analysis assumed that the dielectric response of amorphous LaAlO$_3$ was identical to that previously determined for crystalline[5] LaAlO$_3$. The results indicated a thickness of around 3350 Å, ~10% more than the target thickness. We then fixed the thickness and permitted *n* and *k* to vary from that of single-crystalline LaAlO$_3$ to better match the experimental results. We performed these measurements several times under several different assumptions: (1) assuming a single layer of amorphous LaAlO$_3$ on Si, (2) assuming a mixed interface between the amorphous LaAlO$_3$ and the Si substrate (our routines always found that this was very small), (3) assuming an SiO$_2$ interlayer between the amor-
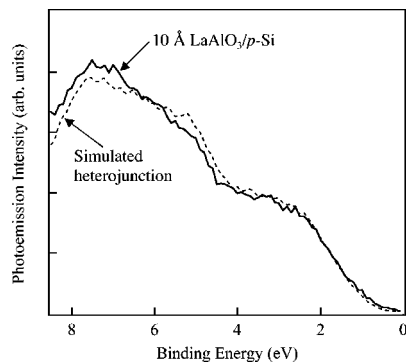
FIG. 3. Simulated VB region in comparison with the measured heterojunction valence band for 10 Å amorphous LaAlO$_3$ on p-Si(001). The simulated VB was produced by shifting and scaling the bare Si(001) spectrum and the thick (150 Å) LaAlO$_3$/Si spectrum and summing the spectra.

phous LaAlO$_3$ and the Si substrate (our routines always found this essentially zero), and (4) assuming a rough surface on the amorphous LaAlO$_3$ (our routines sometimes found this value to exceed 100 Å, but the improvement in rms error was small). The results always indicated virtually no absorption for energies below 6.1–6.3 eV. While we note that very small levels of absorption may be difficult to observe by this technique, we conclude that the bandgap of this material is 6.2±0.1 eV. This value is in fairly good agreement with Lu *et al.*,[8] who reported a bandgap of 6.55 eV for amorphous LaAlO$_3$ on fused silica.

As a check of the XPS method, we simulated the VB spectra of the heterojunctions by shifting and summing the appropriately weighted spectra for Si(001) and thick (150 Å) LaAlO$_3$. Both of the spectra are shown in Fig. 2. These spectra were shifted in energy so that the Si 2p and the Al 2p binding energies matched those of the heterojunctions. The spectra were then scaled so that the Si 2p and the Al 2p areas matched the heterojunctions areas. The adjusted spectra were then summed to simulate the heterojunction VB. Figure 3 shows the simulated VB in comparison with the experimentally measured heterojunction for a 10-Å-thick LaAlO$_3$/p-Si heterojunction. There was good agreement between such simulations and the measured XPS spectra for all heterojunctions.

Figure 4 shows the band diagram for LaAlO$_3$ on n- and p-type silicon. Si 2p centroids in the majority of the films fall at the BE expected for FL pinning at 0.8 eV above the VBM, but a minority fall at other energies. This suggests FL
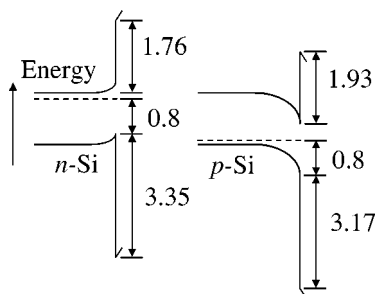
pinning. The experimentally measured VB and CB values are in good agreement with the theoretical predictions of Peacock and Robertson.[10,11] The theoretical predictions have estimated a CBO of 1.0 to 2.1 eV and a VBO of 1.9 to 3.5 eV for single-crystalline-LaAlO$_3$ on silicon.[10,11] We have experimentally measured a CBO of 1.8±0.2 eV and a VBO of 3.2±0.1 eV for amorphous LaAlO$_3$ on silicon. These band-offset values meet the requirements for an alternative gate dielectric as suggested by ITRS[12] and make amorphous LaAlO$_3$ a candidate material for the replacement SiO$_2$ in Si-based MOSFETs.

FIG. 4. Band diagrams for amorphous LaAlO$_3$/Si(001) heterojunctions for both n- and p-type silicon. Energies are in eV.

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