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The Interface between Single Crystalline (001) LaAlO₃ and (001) Silicon

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Atomic resolution high-angle annular dark-field imaging in scanning transmission electron microscopy is used to determine atomic arrangements at LaAlO₃/Si interfaces, which were obtained by growing Si films epitaxially on (001) LaAlO₃ single crystals. An unusual 3 × 1 interface reconstruction, in which every third La column is removed from the interface plane, is observed. The interface atomic structure is discussed in the context of electrically favorable interfacial bonding between the ionic oxide and Si. [DOI: 10.1143/JJAP.44.L617]

KEYWORDS: high-angle annular dark-field imaging, high-k gate dielectrics, oxide/semiconductor interfaces, scanning transmission electron microscopy

Further scaling of complementary metal-oxide–silicon field-effect transistors (CMOS) may require the use of gate dielectrics with a higher dielectric constant (k) than SiO₂. Ultimately, interfaces between Si and high-k gate dielectrics need to be atomically abrupt. Oxides with the perovskite structure are attractive, because of their high k values.¹ Many research efforts to epitaxially integrate perovskites with semiconductors have focused on SrTiO₃;²–⁶ however, SrTiO₃ is not thermally stable in contact with Si⁷ and its tiny conduction band offset with Si causes high leakage currents.⁸ The perovskite LaAlO₃ has a dielectric constant of 24,⁹ a bandgap of 5.6 eV,¹⁰ large band offsets with Si¹¹ and is thermally stable in contact with Si under standard CMOS processing conditions.¹² In contrast to (001) SrTiO₃, stoichiometric (001) LaAlO₃ surfaces are polar and LaAlO₃/Si interfaces may have a very different structure and properties. Epitaxial growth of LaAlO₃ on Si has not yet been achieved, although relatively small lattice mismatch with (001) Si of +1.3% (defined as (a₁−a₃)/a₃, where a₁ and a₃ are the lattice parameters of Si and pseudocubic LaAlO₃, respectively, and [100] LaAlO₃ || [110] Si). Experimental studies have focused on amorphous or polycrystalline LaAlO₃ layers.¹¹–¹³–¹⁵

In this letter, we study direct LaAlO₃/Si interfaces obtained by molecular beam epitaxy (MBE) of Si on (001) LaAlO₃ single crystals with the goal to acquire an improved understanding of the interface. Conventional high-resolution transmission electron microscopy (HRTEM) and atomic resolution high-angle annular dark-field (HAADF) imaging are used to characterize the interface atomic structure.

Substrates were commercial (001) LaAlO₃ single crystals¹⁶ with back sides coated with 2000 Å of Ti. Samples were boiled for 15 min in de-ionized water and blown dry with N₂. The base pressure of the MBE system (DCA Instruments, Inc.) was less than 1.2 × 10⁻⁸ Torr with both the electron-beam-heated Si source and the substrate hot. The substrate was heated in vacuum to temperatures between 800 and 950°C for deposition and exposed to a Si flux for 20 min, which resulted in ~170 nm thick films. In situ reflection high-energy electron diffraction (RHEED) showed a three-dimensional island (Volmer–Weber) growth. After growth, the films were cooled in vacuum. Selected samples were annealed at 900°C for 20 s at 900, 950 and 1025°C. Cross-section transmission electron microscopy samples were prepared by standard techniques. HRTEM and HAADF imaging were performed using a Tecnai F30U TEM with ultra-twin objective lens (Cs = 0.52 nm), operated at 300 kV. For HAADF imaging, the microscope was operated in scanning (STEM) mode.

HRTEM (Fig. 1) shows that the LaAlO₃/Si interface is free of reaction layers. The orientation relationship is described by (001) LaAlO₃ || (001) Si and [100] LaAlO₃ || [110] Si. Twins and stacking faults (black arrow in Fig. 1) are characteristic for Volmer–Weber type growth on insulators.¹⁸ Except for occasional steps of one unit cell height (~3.8 Å) that accommodate the miscut of the substrate surface, the Si/LaAlO₃ interface appears atomically flat in HRTEM. Images along several zone axes show that the steps are parallel to (100) LaAlO₃. Weak periodic changes in the image contrast along the interface are occasionally seen for certain defocus/thickness values (white arrows in Fig. 1).

HAADF images of the LaAlO₃/Si interface recorded along [100] LaAlO₃ are shown in Fig. 2. HAADF images are not subject to contrast reversals, and atomic column positions are obtained directly from the image.⁹ For thin samples, the image contrast is approximately proportional to the atomic number Z². The difference in Z between La (57),...
Al (13), and O (8) causes the Al–O column intensity in LaAlO$_3$ to appear weak in comparison with La columns. O-only columns do not contribute significantly to the image contrast. Some areas appear atomically flat [Figs. 2(b) and (d)], while large open yellow circles La. Small filled red circles indicate likely oxygen positions, which are not visible in HAADF. (e) Reconstructed interface region with shift of the Si lattice by 1/2 unit cell parallel to the interface (average of two images). (f) Region showing that a shift of the Si lattice is required by the overgrowth over a LaAlO$_3$ surface step (unprocessed image).

Fig. 2. HAADF images of the LaAlO$_3$/Si interface along [100]$_{LaAlO_3}$ showing a 3 × 1 interface reconstruction. The inset in (a) shows a magnified image with two Al–O columns indicated by arrows. The block arrow in (b) indicates an interfacial step of one unit cell height. Images (a) and (b) are unprocessed. Figures (c) and (d) show magnified images (averages of 6 and 9 images, respectively) along two perpendicular directions of the reconstruction with overlays that show the atom positions. Medium filled blue circles indicate Al–O atoms, medium open blue circles Si, and large open yellow circles La. Small filled red circles indicate likely oxygen positions, which are not visible in HAADF. (e) Reconstructed interface region with shift of the Si lattice by 1/2 unit cell parallel to the interface (average of two images). (f) Region showing that a shift of the Si lattice is required by the overgrowth over a LaAlO$_3$ surface step (unprocessed image).

Fig. 3. (a) Interface model consistent with the HAADF images. The model leaves no Si dangling bonds but is not charge compensated (see text). (b) Same model as in (a) shown in projection along [100]. (c) Model with extra Si atoms adjacent to the missing La-columns. (d) Charge compensated model without Si dangling bonds, requiring an extra Si atom per every two La–O surface unit cells along [100]. Contrast that may represent single Si atoms similar to model (c) and (d) is occasionally observed in the images. All directions are referred to pseudocubic LaAlO$_3$. 

While surface reconstructions are frequently observed, few reports exist of intrinsic reconstructions of heterointerfaces. Charged polar surfaces can be stabilized by surface reconstruction. As discussed below, a 3 × 1 surface...
reconstruction with missing La columns would not yield a stable surface without another charge compensation mechanism, for example adsorption of $\text{H}^+$. RHEED patterns recorded of the LaAlO$_3$ surfaces before deposition showed no surface reconstruction. More sensitive surface studies should, however, be employed to determine whether the reconstruction is intrinsic to this interface or reflects a preserved surface reconstruction.

Interface atomic structures for electrically favorable interfaces have recently been discussed for high-$k$/Si interfaces. Ideally, bonding at the interface satisfies the valence requirements of the hybridized $\text{Si}$ and $\text{O}$ atoms, and give rise to a metallic interface. Each surface atom of a (001) $\text{Si}$ surface has two dangling bonds, one of which can be removed by a $2 \times 1$ dimer surface reconstruction. In bulk LaAlO$_3$, each LaO layer donates 1/2 electron to each of the two adjacent AlO$_2$ layers (assuming an ideal cubic crystal). To be stable, a LaO surface (unreconstructed) requires a mechanism that removes 1/2 electron per surface unit cell.

Figure 3 illustrates the difficulties in constructing electrically favorable LaAlO$_3$/Si interfaces that are consistent with the HAADF images, using one of the observed interface variants [Figs. 2(c) and (d)] as an example. The observed reconstruction causes the La–O surface layer to lack 1/2 electron per unreconstructed surface unit cell. Ideally, bonding with Si would provide the necessary charge compensation. The models [Figs. 3(a)–(c)] avoid dangling bonds, but charge compensation requires additional species. For example, the interface model in Fig. 3(a) allows for the donation of 1 electron per oxide surface unit cell from the Si dangling bonds. This over-satisfies the electron counting requirement by 1/2 electron per unreconstructed surface unit cell, although it could be satisfied with additional species such as partially filled interfacial $\text{OH}^-$ or extra O (not visible in HAADF). Other possible interface atomic arrangements also require additional compensation mechanisms, which are likely difficult to realize experimentally. The model in Fig. 3(c) over-satisfies the electron counting requirements by 1/2 electron per unreconstructed surface unit cell. The model shown in Fig. 3(d) satisfies all requirements, but requires that Si bonds to both La and O. It is thus very likely that real (001) LaAlO$_3$/Si interfaces contain Si dangling bonds or that the valence requirements are not satisfied.

Even more importantly, simple electron counting models make it difficult to construct any electrically favorable La–O terminated interface without additional passivation mechanisms. Unreconstructed LaO (AlO$_2$) surfaces, as proposed in the literature, require the donation (acceptance) of 1/2 electron per surface unit cell to (from) the semiconductor and do not meet the conditions for charge neutrality. Given their similar charge compensation problems, the experimentally observed $3 \times 1$ reconstructed interface may be favored over an unreconstructed LaO terminated interface if Si–O bonds are energetically preferred. Al–O terminated interfaces may yield charge compensated interfaces with no dangling bonds if three oxygens were removed per four surface unit cells (AlO$_{1.25}$ surface stoichiometry). Interfaces constructed from charge-neutral surfaces, i.e., with 1/6 of the La removed from a La–O surface or 1/4 O from an Al–O surface, may yield electrically favorable interfaces, if the Si dangling bonds were passivated with oxygen or hydrogen, respectively.

In summary, the interfacial atomic arrangements observed by HAADF imaging can be used for further structure refinements, calculations of the band structure and the electrical properties. We have shown that charge compensated (001) LaAlO$_3$/Si interfaces, constructed using simple electron counting models, are difficult to realize experimentally.

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