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The Interface between Single Crystalline (001) $LaAlO_3$ 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 $LaAlO_3$/Si interfaces, which were obtained by growing Si films epitaxially on (001) $LaAlO_3$ 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 SiO_2. 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 $SrTiO_3$:[2–6)] however, $SrTiO_3$ is not thermally stable in contact with Si[7)] and its tiny conduction band offset with Si causes high leakage currents.[8)] The perovskite $LaAlO_3$ has a dielectric constant of 24,[9)] a bandgap of 5.6 eV,[10)] large band offsets with Si[11)] and is thermally stable in contact with Si under standard CMOS processing conditions.[12)] In contrast to (001) $SrTiO_3$, stoichiometric (001) $LaAlO_3$ surfaces are polar and $LaAlO_3$/Si interfaces may have a very different structure and properties. Epitaxial growth of $LaAlO_3$ on Si has not yet been achieved, despite its relatively small lattice mismatch with (001) Si of +1.3% (defined as $(a_{Si} - a_{LaAlO_3})/a_{LaAlO_3}$, where a_{Si} and a_{LaAlO_3} are the lattice parameters of Si and pseudocubic $LaAlO_3$, respectively, and [100] $LaAlO_3$ ‖ [110] Si). Experimental studies have focused on *amorphous* or *polycrystalline* $LaAlO_3$ layers.[11,13–15)]

In this letter, we study direct $LaAlO_3$/Si interfaces obtained by molecular beam epitaxy (MBE) of Si on (001) $LaAlO_3$ 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) $LaAlO_3$ single crystals[16)] with backsides coated with 2000 Å of Ti. Samples were boiled for 15 min in de-ionized water[17)] and blown dry with N_2. 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 mode. After growth, the films were cooled in vacuum. Selected samples were annealed in N_2 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 ($Cs = 0.52$ mm), operated at 300 kV. For HAADF imaging, the microscope was operated in scanning (STEM) mode.

HRTEM (Fig. 1) shows that the $LaAlO_3$/Si interface is free of reaction layers. The orientation relationship is described by (001) $LaAlO_3$ ‖ (001) Si and [100] $LaAlO_3$ ‖ [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/$LaAlO_3$ interface appears atomically flat in HRTEM. Images along several zone axes show that the steps are parallel to $\langle 100 \rangle_{LaAlO_3}$. 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 $LaAlO_3$/Si interface recorded along [100] $LaAlO_3$ are shown in Fig. 2. HAADF images are not subject to contrast reversals, and atomic column positions are obtained directly from the image.[19)] For thin samples, the image contrast is approximately proportional to the atomic number Z^2. The difference in Z between La (57),

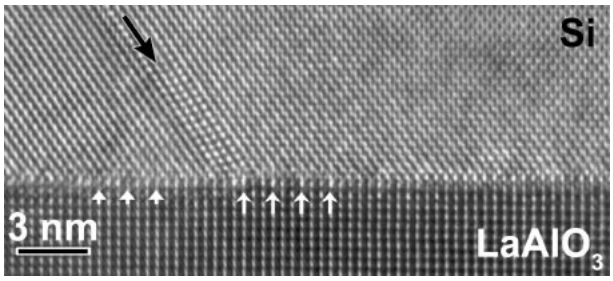

Fig. 1. HRTEM micrograph of the $LaAlO_3$/Si interface (grown at 850°C and annealed at 900°C) along $[100]_{LaAlO_3}$. The black arrow indicates a twin in the Si film. White arrows indicate regions along the interface that show periodic contrast changes. Note that the contrast change reverses along the interface, from two-dark-one bright (right) to two-bright-one-dark (left). This is likely due to changes in the TEM sample thickness.

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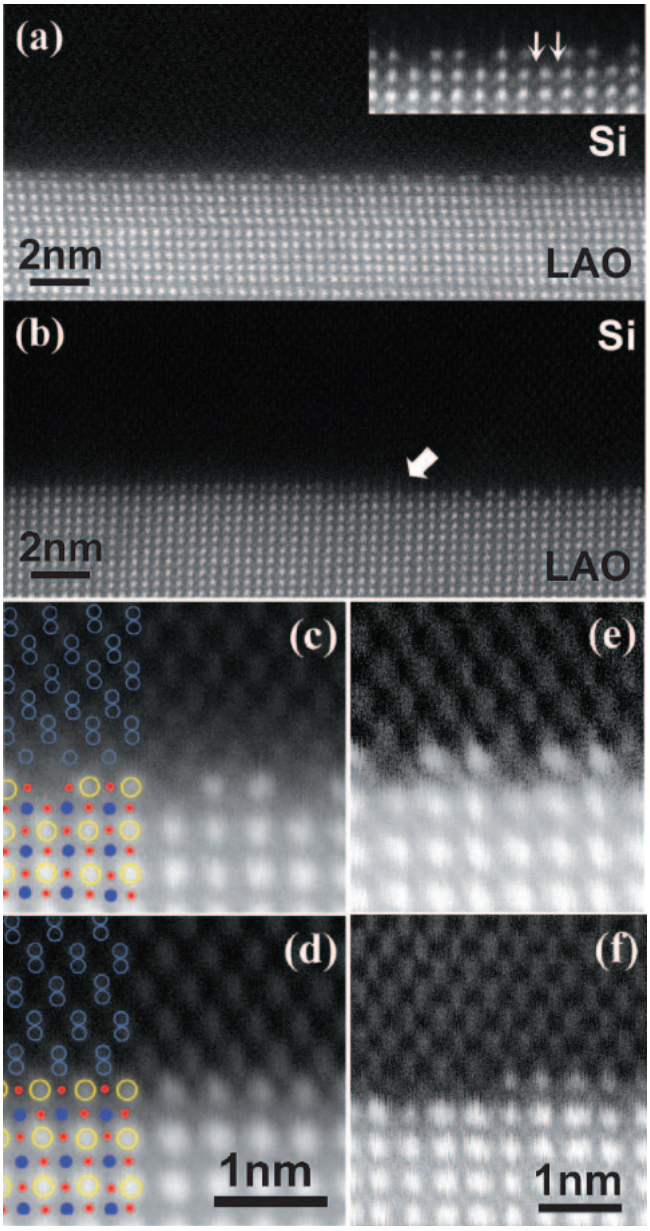

Fig. 2. HAADF images of the $LaAlO_3$/Si interface along $[100]_{LaAlO_3}$ showing a 3×1 interface reconstruction. The inset in (a) shows a magnified image with two Al–O columns indicated by arrows. The block arrow in (b) indicates an interfacial step of one unit cell height. Images (a) and (b) are unprocessed. 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).

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 others show an interface reconstruction with every third La column removed from the interface plane along [100] $LaAlO_3$ [Figs. 2(a)–2(c) and 2(e)]. The inset in Fig. 2(a) shows intensity maxima at the positions of the Al–O columns, including near the missing La columns. An identical interface reconstruction is observed for all deposition and annealing temperatures, respectively. Intensity profiles show that the intensity of the La columns in regions that appear unreconstructed is about two-thirds of that of the La columns in adjacent substrate. Thus they likely contain missing La columns along the direction normal to the electron beam. The change in orientation coincides frequently with interface steps [Fig. 2(b)]. Occasional residual contrast in the missing La column positions [Fig. 2(f)] is likely due to a step within the TEM foil. Figures 2(c) and (d) show the cation positions obtained from the images parallel (denoted [100]) and perpendicular (denoted [010]) to the missing La-columns, respectively. The terminating Si layer appears as a single Si column along [100] and as a dumbbell along [010] [see schematic in Fig. 3(a)]. Some weak contrast that may correspond to an extra Si plane is occasionally visible, and is incorporated in the models in Figs. 3(c) and (d). The Si lattice is shifted by half a unit cell along ⟨100⟩ in some regions [Fig. 2 (e)], likely due to surface steps [Fig. 2(f)]. Thus more than one low-energy interface configuration may exist. The positions of the O atoms must be inferred from bonding arguments, which will be discussed below.

While surface reconstructions are frequently observed, few reports exist of intrinsic reconstructions of heterointerfaces.[20] Charged polar surfaces can be stabilized by surface reconstruction.[21] As discussed below, a 3×1 surface

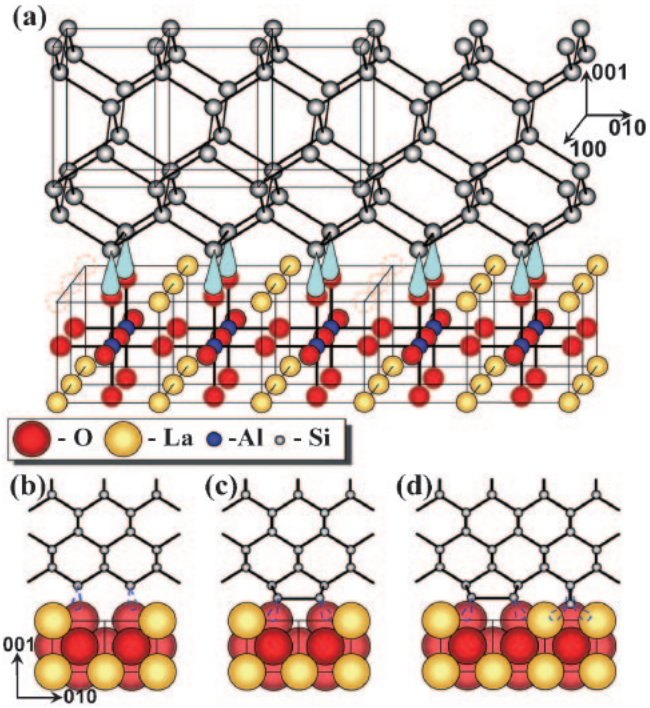

Fig. 3. (a) Interface model consistent with the HAADF images. The model leaves no Si dangling bonds but is not charge compensated (see text). (b) Same model as in (a) shown in projection along [100]. (c) Model with extra Si atoms adjacent to the missing La-columns. (d) Charge compensated model without 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 $LaAlO_3$.

reconstruction with missing La columns would not yield a stable surface without another charge compensation mechanism, for example adsorption of 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.[22] Ideally, bonding at the interface satisfies the valence requirements[23] and produces no dangling Si bonds. Dangling bonds are half-filled (with one electron) sp^3 hybrids, and give rise to a metallic interface.[24] Each surface atom of a (001) Si surface has two dangling bonds, one of which can be removed by a 2×1 dimer surface reconstruction.[24] In bulk $LaAlO_3$, each LaO layer donates $1/2$ electron to each of the two adjacent AlO_2 layers (assuming an ideal ionic crystal). To be stable, a LaO surface (unreconstructed) requires a mechanism that removes $1/2$ electron per surface unit cell.[21]

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 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 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,[25,26] 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.[23] Given their similar charge compensation problems, the experimentally observed 3×1 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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1) D. G. Schlom and J. H. Haeni: MRS Bull. **27** (2002) 198.
2) R. A. McKee, F. J. Walker and M. F. Chisholm: Phys. Rev. Lett. **81** (1998) 3014.
3) K. Eisenbeiser, J. M. Finder, Z. Yu, J. Ramdani, J. A. Curless, J. A. Hallmark, R. Droopad, W. J. Ooms, L. Salem, S. Bradshaw and C. D. Overgaard: Appl. Phys. Lett. **76** (2000) 1324.
4) C. J. Först, C. R. Ashman, K. Schwarz and P. E. Blöchl: Nature **427** (2004) 53.
5) P. W. Peacock and J. Robertson: Appl. Phys. Lett. **83** (2003) 5497.
6) X. Zhang, A. A. Demkov, H. Li, X. Hu, Y. Wei and J. Kulik: Phys. Rev. B **68** (2003) 125323.
7) K. J. Hubbard and D. G. Schlom: J. Mater. Res. **11** (1996) 2757.
8) S. A. Chambers, Y. Liang, Z. Yu, R. Droopad, J. Ramdani and K. Eisenbeiser: Appl. Phys. Lett. **77** (2000) 1662.
9) R. Schwab, R. Sporl, P. Severloh, R. Heidinger and J. Halbritter: Inst. Phys. Conf. Ser. **158** (1997) 61.
10) S. G. Lim, S. Kriventsov, T. N. Jackson, J. H. Haeni, D. G. Schlom, A. M. Balbashov, R. Uecker, P. Reiche, J. L. Freeouf and G. Lucovsky: J. Appl. Phys. **91** (2002) 4500.
11) L. F. Edge, D. G. Schlom, S. A. Chambers, E. Cicerrella, J. L. Freeouf, B. Hollander and J. Schubert: Appl. Phys. Lett. **84** (2004) 726.
12) S. Stemmer and D. G. Schlom: in *Nano and Giga Challenges in Microelectronics*, eds. J. Greer, A. Korkin and J. Labanowski (Elsevier, Amsterdam, 2003) p. 129.
13) A. D. Li, Q. Y. Shao, H. Q. Ling, J. B. Cheng, D. Wu, Z. G. Liu, N. B. Ming, C. Wang, H. W. Zhou and B. Y. Nguyen: Appl. Phys. Lett. **83** (2003) 3540.
14) B. E. Park and H. Ishiwara: Appl. Phys. Lett. **82** (2003) 1197.
15) L. F. Edge, D. G. Schlom, R. T. Brewer, Y. J. Chabal, J. R. Williams, S. A. Chambers, C. Hinkle, G. Lucovsky, Y. Yang, S. Stemmer, M. Copel, B. Holländer and J. Schubert: Appl. Phys. Lett. **84** (2004) 4629.
16) G. W. Berkstresser, A. J. Valentino and C. D. Brandle: J. Cryst. Growth **128** (1993) 684.
17) B. Kropman and D. H. A. Blank: personal communication.
18) V. Narayanan, S. Guha, N. A. Bojarczuk and F. M. Ross: J. Appl. Phys. **93** (2003) 251.
19) S. J. Pennycook: in *Advances in Imaging and Electron Physics*; *Vol. 123* (2002) p. 173.
20) D. Loretto, J. M. Gibson and S. M. Yalisove: Phys. Rev. Lett. **63** (1989) 298.
21) P. W. Tasker: J. Phys. C **12** (1979) 4977.
22) P. W. Peacock and J. Robertson: Phys. Rev. Lett. **92** (2004) 057601.
23) W. A. Harrison, E. A. Kraut, J. R. Waldrop and R. W. Grant: Phys. Rev. B **18** (1978) 4402.
24) W. A. Harrison: *Electronic Structure And The Properties of Solids* (Dover, New York, 1989).
25) J. Robertson and P. W. Peacock: Mater. Res. Soc. Symp. Proc. **786** (2004) 23.
26) J. Robertson and P. W. Peacock: Phys. Status Solidi B **241** (2004) 2236.