

# Band offsets at amorphous-crystalline Al<sub>2</sub>O<sub>3</sub>–SrTiO<sub>3</sub> oxide interfaces

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2D electron gases (2DEGs) formed at oxide interfaces provide a rich testbed for fundamental physics and device applications. While the discussion of the physical origins of this phenomenon continues, the recent discovery of oxide 2DEGs at non-epitaxial interfaces between amorphous and crystalline oxides provides useful insight into this debate. Furthermore, using amorphous oxides offers a low-cost route towards realizing 2DEGs for device applications. In this work, the band offsets of a simple model system of an amorphous-crystalline oxide interface are investigated. The model system consists of amorphous Al<sub>2</sub>O<sub>3</sub> grown on single-crystalline (001) SrTiO<sub>3</sub>. X-ray photo-electron spectroscopy is employed to study the chemical states, bandgap, and band offsets at the interface. The density of ionic defects near the interface is found to be below the detection limit, and the interface is found to be insulating. Analysis of the relative band structure yields significant interfacial barriers, exceeding 1.05 eV for holes and 2.0 eV for electrons. The barrier for holes is considerably larger than what is known for related material systems, outlining the promise of using amorphous Al<sub>2</sub>O<sub>3</sub> as an effective and simple insulator, an important building block for oxide-based field effect devices. *Published by AIP Publishing*. https://doi.org/10.1063/1.5030119

## I. INTRODUCTION

The first observation of 2D electron gases (2DEGs) at an epitaxial interface between two insulating oxides<sup>1</sup> has quickly led to the discovery of rich and unexpected physics.<sup>2–4</sup> These findings have sparked tremendous interest in multiple communities, ranging from fundamental physics to materials science and to the engineering of various electronic and optoelectronic devices.<sup>5–10</sup>

The underlying physics of 2DEG formation has been narrowed down to two leading mechanisms: a polarization mechanism and an ionic defect mechanism. The polarization mechanism, or the *polar catastrophe*, argues that polar discontinuity at the interface, between a non-polar substrate, typically SrTiO<sub>3</sub>, and a polar epitaxial overlayer such as LaAlO<sub>3</sub>, results in a diverging potential across the latter. The potential divergence is mitigated by an electronic reconstruction that often occurs above a critical thickness. In this case, 1/2 an electron per unit cell is transferred from the top surface to the interface, where it occupies the empty Ti 3d-orbitals of SrTiO<sub>3</sub>.<sup>11</sup> The recent observation of the long-sought 2D *hole* gas at this top interface<sup>12</sup> further supports the polarization mechanism.

Alternatively, the ionic mechanism highlights the role of defects as the cause of 2DEGs, typically defects that can be formed during the epitaxial growth of the overlayer<sup>13</sup> (e.g., LaAlO<sub>3</sub>). Some possible defects can act as dopants near the surface of SrTiO<sub>3</sub>. The most studied suspect in this context is the oxygen vacancy, a well-known electron donor in SrTiO<sub>3</sub>. Oxygen vacancies were shown to form readily at typical growth conditions of LaAlO<sub>3</sub>,<sup>14</sup> resulting in interface conduction.<sup>15–18</sup> Additional ionic suspects for the formation of 2DEGs are ions such as La, which can diffuse into SrTiO<sub>3</sub>.

during epitaxial growth, where they function as dopants,<sup>19–22</sup> as well as other electronically active defects.<sup>23,24</sup> Ample experimental evidence supporting both mechanisms suggests that there is no single culprit behind the 2DEG phenomena.

To make things more interesting, it was later discovered<sup>25,26</sup> that 2DEGs can be formed at non-epitaxial interfaces between a single-crystal substrate and amorphous oxides. Chemical evidence correlated the presence of 2DEGs and interfacial SrTiO<sub>3</sub> oxygen vacancies. This observation demonstrates that similar 2DEGs can be obtained in a material system where the polarization mechanism is not possible, due to the absence of long-range order. These observations do not categorically rule out the polarization mechanism, rather they underscore the complexity of the problem and highlight the importance of the surface chemistry, oxidation states, and interface electrostatics. A key aspect of this picture is the relative offsets between the bands at the interface. This aspect has been thoroughly studied in polar/non-polar *epitaxial* interfaces such as GdTiO<sub>3</sub>/SrTiO<sub>3</sub>,<sup>27,28</sup> γ-Al<sub>2</sub>O<sub>3</sub>/ SrTiO<sub>3</sub>,<sup>29,30</sup> NdTiO<sub>3</sub>/SrTiO<sub>3</sub>,<sup>31,32</sup> LaNiO<sub>3</sub>/SrTiO<sub>3</sub>,<sup>27</sup> SmTiO<sub>3</sub>/ SrTiO<sub>3</sub>,<sup>28</sup> LaCrO<sub>3</sub>/SrTiO<sub>3</sub>,<sup>33</sup> and LaAlO<sub>3</sub>/SrTiO<sub>3</sub>,<sup>22,34–37</sup> providing valuable physical insight, such as the existence<sup>33</sup> or absence<sup>29,38</sup> of polarization-induced internal fields, substrate band bending,<sup>29</sup> and effects of ion intermixing<sup>22</sup> and oxygen vacancies.<sup>36</sup>

Despite this wealth of data on crystalline epitaxial interfaces, the band offsets at amorphous/crystalline oxide interfaces have not been addressed. These systems allow a case study of an electronic structure of interfaces in the absence of polar fields. Motivated by this knowledge gap, we study the surface chemistry, electronic structure, and relative band offsets at an amorphous-crystalline interface between Al<sub>2</sub>O<sub>3</sub> and SrTiO<sub>3</sub> (STO). This structure is further gaining recent attention as a tunneling junction in spintronic devices,<sup>39,40</sup>

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FIG. 1. Tapping mode AFM image of the surface of a  $5 \times 5 \ \mu m^2$  region of the surface of a thick Al<sub>2</sub>O<sub>3</sub> layer (10 nm) on undoped STO.

where better understanding of the electronic structure is expected to improve performance.

#### II. EXPERIMENTAL

TiO<sub>2</sub> termination was performed on (001) undoped, 0.05% and 0.5%(wt) Nb-doped STO substrates (Shinkosha Ltd.) based on the "extended Arkansas" method.<sup>41</sup> This process started with solvent sonication cleaning, followed by a 3:1 HCl-HNO<sub>3</sub> treatment and a two-step anneal, starting with 1000°C for 1 h in air and completed with 650°C for 30 min in flowing O<sub>2</sub>. Amorphous Al<sub>2</sub>O<sub>3</sub> layers were grown by atomic layer deposition (ALD, Ultratech/Cambridge Nanotech Fiji G2) using trimethyl-aluminum (TMA) and water as the precursors at a substrate temperature of 300 °C. 4 and 10 nm thick layers were grown: the thin layer puts both the Al<sub>2</sub>O<sub>3</sub> and the STO substrate within the probing depth of x-ray photoelectron spectroscopy (XPS), whereas only Al<sub>2</sub>O<sub>3</sub> is probed in the thick Al<sub>2</sub>O<sub>3</sub> layer. The thicknesses of the layers were found to be in close agreement with the nominal values using x-ray reflectivity measurements. These layers are referred to as Thin Al<sub>2</sub>O<sub>3</sub> and Thick Al<sub>2</sub>O<sub>3</sub> henceforth.

An atomic force microscopy (AFM, Asylum MFP-3D Infinity) image was acquired in the tapping mode from the

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surface of the Thick Al<sub>2</sub>O<sub>3</sub> grown on an undoped STO substrate (Fig. 1). The observation of long range atomically flat terraces with atomic height steps from the underlying STO substrate indicates that the roughness of the thin Al<sub>2</sub>O<sub>3</sub> layer is well below the ~0.4 nm step height. No evidence of Al<sub>2</sub>O<sub>3</sub> crystallinity was found in x-ray diffraction data acquired from the thick sample (Fig. S1, supplementary material). XPS (5600 Multi-Technique system, PHI) spectra were acquired using a monochromated Al K $\alpha$  source (1486.6 eV) and a pass energy of 11.75 eV. Data were fit with the CasaXPS software using a Shirley background and a 30% Lorentzian-Gaussian ratio.

### **III. RESULTS AND DISCUSSION**

The Ti  $2p_{3/2}$  XPS spectrum acquired from the thin  $Al_2O_3$  and bare undoped STO samples [Fig. 2(a)] shows a well-behaved +4 state,<sup>42</sup> and no +3 oxidation states are observable at lower binding energies,<sup>26,43</sup> further validating the surface preparation procedure. The thick  $Al_2O_3$  layer is used for studying the properties of  $Al_2O_3$  without interference from the substrate. The Al 2p spectrum [Fig. 2(b)] shows well-behaved features that are fit with one doublet having a  $0.4 \,\text{eV}$  separation,<sup>44</sup> showing a single oxidation state consistent with  $Al_2O_3$ .

Analysis of the O 1s region (Fig. 3) reveals a major component that is ascribed to  $Al_2O_3$  ("Peak 1"), and a minor moiety ("Peak 2"), attributed to surface contamination. The uncertainty in the position of the small contamination peak has a negligible effect on the position of the major O 1s component of the  $Al_2O_3$  film.<sup>46</sup> The distance of the onset of the energy loss tail<sup>47,48</sup> from the major O 1s ( $Al_2O_3$ ) peak yields a bandgap of  $6.6 \pm 0.2 \text{ eV}$  (denoted by a horizontal arrow in the inset of Fig. 3). This value is in agreement with previous reports for amorphous  $Al_2O_3$ .<sup>44,48,49</sup>

Al contacts<sup>50</sup> were deposited on the corners of the undoped thin alumina on the SrTiO<sub>3</sub> sample (e-beam deposition) after scratching it to contact the buried interface.<sup>51</sup> The resistance of the film was beyond the measurement limit (>5 MΩ); we interpret this limit to indicate a sheet carrier density below  $10^{11}$  cm<sup>-2</sup>. This observation is in agreement with the absence of the Ti<sup>+3</sup> signal in the Ti 2p<sub>3/2</sub> spectrum acquired from the Al<sub>2</sub>O<sub>3</sub>-STO interface (thin Al<sub>2</sub>O<sub>3</sub>), Fig. 2(a). Similar observations were also made by Susaki *et al.* using hard x-ray photoemission spectroscopy (HAXPS) at polar LaAlO<sub>3</sub>-STO interfaces.<sup>37</sup> Considering the background, we conclude that Ti<sup>+3</sup> could account for as much as 1% of the



FIG. 2. (a) Ti  $2p_{3/2}$  XPS spectra of the clean surface of a bare substrate (blue) superimposed on the Ti  $2p_{3/2}$  spectrum, obtained from underneath the thin Al<sub>2</sub>O<sub>3</sub> (4 nm) layer (red). (b) Al 2p spectrum of a Thick Al<sub>2</sub>O<sub>3</sub> (10 nm).



FIG. 3. O 1s spectrum of a Thick  $Al_2O_3$  (10 nm). The inset shows a magnified region of the energy loss tail, taken from the dashed blue rectangle. The vertical lines represent the centroid of the major O 1s peak (brown) and the intersection of the linear fit of the loss tail with the background<sup>48</sup> (black). The distance between the lines (blue horizontal arrow) denotes the bandgap of  $Al_2O_3$ .

signal. A previous report of Al<sub>2</sub>O<sub>3</sub>-STO grown by ALD has shown a sheet carrier density of  $3 \times 10^{12}$  cm<sup>-2</sup> and corresponding Ti<sup>+3</sup> features, which were ascribed to surface reduction by the TMA precursor during the 300 °C ALD process.<sup>26</sup> While the growth temperature employed here is similar, we attribute the absence of surface reduction here to variations in growth and control parameters between the different ALD systems. The ability to obtain an insulating interface without significant oxygen vacancies is useful for several applications; insulator-STO interfaces with low ionic defect densities are sought for various devices, and currently, complex routes are employed to form such interfaces.<sup>52,53</sup>

Next, we turn to analyze the band offsets at the interface. Alignment of the energy scales of the different samples was done as follows: First, the energy scales of both the thick and thin Al<sub>2</sub>O<sub>3</sub> layers were aligned so that the Al  $2p_{3/2}$  peak of each is positioned at 74.4 eV (Ref. 44) (dashed vertical line in Fig. 4). The energy scale of the bare STO substrate was then aligned as such that the Ti 2p<sub>3/2</sub> peak is at the same energy as the features acquired from underneath the thin  $Al_2O_3$  layer (Fig. 4). This systematic alignment of the energy scale allows the direct comparison of the valence band edges<sup>54-56</sup> of Al<sub>2</sub>O<sub>3</sub> and STO, yielding the valence band offset of  $1.35 \pm 0.2 \text{ eV}$  at the Al<sub>2</sub>O<sub>3</sub>-undoped STO interface. Kormondy and coworkers reported an offset of 0.9 eV for crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, epitaxially grown on STO,<sup>30</sup> and while y-Al<sub>2</sub>O<sub>3</sub> has a different band structure compared to the amorphous phase, we note the similarity of these values.

This analysis was further extended to study 0.05 and 0.5%(wt) Nb-doped STO substrates and resulted in valence band offsets of  $1.05 \pm 0.2$  and  $1.4 \pm 0.2 \text{ eV}$ , respectively [Figs. 4(b) and 4(c), Table I]. These valence band offsets are considerably larger than the reported values of 0.0-0.6 eV for the epitaxial LaAlO<sub>3</sub>-STO interface.<sup>34,36,37</sup> Schütz *et al.* reported a ~0 eV valence band offset for epitaxial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-STO and a large ~3.8 eV conduction band offset.<sup>29</sup> The larger valence band offset measured here suggests that amorphous



FIG. 4. Band alignment analysis of the  $Al_2O_3$ -STO interface. The Al 2p, Ti  $2p_{3/2}$ , and valence band (VB) spectra of a Bare STO substrate, Thin  $Al_2O_3$  (4nm), and Thick  $Al_2O_3$  (10nm) are shown for shown for (a) undoped, (b) 0.05%(wt), and (c) 0.5%(wt) Nb-doped STO substrates. The dashed grey line represents the energy alignment to an energy of 74.4 eV. The Thick  $Al_2O_3$  data (green triangles) are duplicated from panel a to panels b and c for clarity.

Al<sub>2</sub>O<sub>3</sub> may be a better insulator than the more common LaAlO<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for field effect devices.<sup>10</sup> This observation highlights the promise of ALD-grown Al<sub>2</sub>O<sub>3</sub> to provide a simple route towards field effect devices based on oxide 2DEGs. We note that while insulating AlO<sub>x</sub> and LaAlO<sub>x</sub> have been previously used for lateral spacers or hard masks,<sup>57–59</sup> they have not been addressed or studied in the current context of barriers and energy alignment. Interestingly, Schütz *et al.* have further reported an ~0.6 eV downward band bending in STO,<sup>29</sup> whereas in the current work, the band bending is estimated to be negligible (Table S1 and discussion therein, Supplementary Material). The absence of band bending here indicates the possible role of the polarity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in bending of the STO bands to compensate for this polar field.

Combining the measured valence band offsets with the bandgap of Al<sub>2</sub>O<sub>3</sub> (6.6 ± 0.2 eV, Fig. 3) and the bandgap of STO (3.2 eV, which does not change over the doping range used here<sup>56</sup>), the conduction band offsets are determined as 2.05, 2.35, and  $2.0 \pm 0.3 \text{ eV}$  for undoped, 0.05%, and 0.5%(wt) Nb–Al<sub>2</sub>O<sub>3</sub> interfaces, respectively (Fig. 5, Table I). An uncertainty range of ±0.2 eV is estimated from the determination of the valence band edge and the bandgap (accumulating to ±0.3 eV when both are factored in), whereas the peaks were fit with uncertainties <0.05 eV. We therefore conclude that substrate doping, within the ranges studied here, has a small effect on the band alignment compared to these uncertainties. The slight deviation of the 0.05%(wt)

TABLE I. Summary of the band offsets of Al2O3 with different STO substrates.

Substrate	Valence band offset $\pm 0.2 \text{ eV}$	Conduction band offset ±0.3 eV
Undoped STO	1.35	2.05
0.05%(wt) Nb	1.05	2.35
0.5%(wt) Nb	1.4	2.0



FIG. 5. Schematic relative band structure at the  $Al_2O_3$ -STO interface for the undoped substrate (Table I).

sample from the others is possibly real, being outside the uncertainty range.

### **IV. CONCLUSION**

Non-polar amorphous  $Al_2O_3$ -STO oxide interfaces prepared by a simple, scalable, low-temperature process were studied. The interface with undoped STO was found to be insulating, with a low density of ionic defects—below the detection limit of XPS. The large bandgap of amorphous  $Al_2O_3$  results in offsets larger than those reported for related material systems, constituting significant interfacial barriers for both holes and electrons. The effect of STO doping on the band offsets is not significant, in the range of 0%–0.5%(wt) Nb doping. These results highlight the potential of  $Al_2O_3$  as an insulator for STO-based oxide electronics, constituting a promising building block for field effect devices.

### SUPPLEMENTARY MATERIAL

See supplementary material for microstructural analysis of  $Al_2O_3$  with x-ray diffraction and discussion of the band bending and built-in potentials, with a summary of the peak parameters from Fig. 4. The entire XPS raw data presented in this work is available in .csv and .xlsx formats as part of the supplementary files. The energy scale was shifted in the same manner as here.

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