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Is -Al2O3 polar?

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Is γ-Al₂O₃ polar?

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Abstract:

Polarity in thin films and polar discontinuities across an interface plays an important role in determining electronic properties. A key example is the conductivity at the LaAlO₃/SrTiO₃ (LAO/STO) interface, which is proposed to originate from the polarity of LAO. As a consequence, the conductivity remains when LAO/STO is subjected to highly oxidizing conditions. Substituting LAO with another nominally polar material γ-Al₂O₃ (GAO) results in an interface conductivity which can be destroyed by annealing in oxygen. We investigate this apparent paradox by revisiting the defect spinel atomic structure of GAO. We show that the polarity is dependent on the distribution of aluminum vacancies which are intrinsically present in GAO to ensure charge neutrality. In particular, certain film thicknesses allow for vacancy distributions that make GAO nominally non-polar along the [001] direction. We further propose that electromigration of aluminum vacancies across atomic layers can alter the polarity, making the GAO film effectively act as a ferroelectric.

Keywords: Polarity; γ-Al₂O₃/SrTiO₃; ferroelectric; 2-dimensional electron gas; aluminum vacancies; oxygen vacancies

1. Introduction: Polarity has profound impact on the properties and applications of surfaces, thin films and heterostructures. If left uncompensated, it causes an increase in the electrostatic potential when the thickness of the polar material is increased in the direction of the polarity. The potential build-up may result in atomic restructuring [1], electric band gradients [2], spontaneous defect formation [2,3] and electron transfer [2]. Surfaces are traditionally classified into three types with respect to their polarity, where type 1 is a non-polar surface with no dipole moment perpendicular to the surface, type 2 has internal dipole moments but no net dipole moment whereas type 3 has a net dipole moment [1]. Type 1 and 2 result in modest surface energies, whereas a type 3 surface has high surface energy and is typically not stable without a substantial reconstruction of the atomic lattice. Such a reconstruction is proposed to be the origin of the conductivity in the type 3/1 heterostructure formed when the polar LaAlO₃ (LAO) is grown epitaxially on the TiO₂-terminated (001) surface of nominally non-polar SrTiO₃ (STO) [2]. The (001) planes of these ABO₃ perovskites can be viewed as alternating AO₂ and BO layers as depicted in Figure 2a. If formal valence charges are assigned to the atoms (Sr^{2+}, Ti^{4+}, La^{3+}, Al^{3+}, O^{2-}), STO is non-polar as it is composed of charge neutral atomic planes, whereas planes with an alternating charge density of ± 1 elementary charge pr. surface unit cell ($\sigma = \pm e/a_{LAO}^2$) make LAO is polar [2]. If the atomic layers are (crudely) approximated as charged continuous planes, the electric field between the planes becomes $E = \sigma/\varepsilon_r\varepsilon_0$, giving rise to an electrostatic potential build-up ($V(z) = \int_{-\infty}^{z} E(z')dz'$), which increases linearly with the LAO thickness (see Figure 2g). Adopting a dielectric constant of $\varepsilon_r = 24$ for LAO [4], the potential build-up is 0.94 V/a_{LAO}. Above a critical thickness of LAO, it becomes energetically favorable to counter the potential build-up by an electron transfer from the top of LAO to the LAO/STO interface where the resulting mobile electrons cause interface conductivity [2]. This explains the sudden insulator-to-metal transition

with increasing LAO thickness observed experimentally [5]. While overly simple, the polarity model has been shown to be qualitatively useful in this [2,6] and other systems [1,7], even if more detailed density-functional based studies are needed to predict the actual density of free carriers resulting from the electron transfer [8].

A recent study compared heterostructures where different non-polar and polar oxide films were grown on STO [9]. By heating up the heterostructures to 950 K and varying the oxygen partial pressure, it was found that at low (< 10⁻²⁰ bar) or high (> 10⁻⁴ bar) oxygen pressure, the conductivity of all heterostructures in thermal equilibrium is dominated by oxygen vacancy donors or acceptors in STO, respectively (see Figure 1). At intermediate partial pressures, however, an oxygen independent contribution to the conductivity was found only for polar films (LAO, NdGaO₃ and (La,Sr)(Al,Ta)O₃ (LSAT)). Results from NdGaO₃ and LSAT can be found in Ref. [9]. As this contribution scales with the polarity of the film and is absent below the critical thickness of LAO, it was attributed to the electron transfer to STO due to the potential build-up. Although γ-Al₂O₃ (GAO) is generally considered to be polar [10], the oxygen-independent conductivity contribution was completely absent. This leads to the conclusion that the origin of the conductivity in GAO/STO is thermodynamically unstable interface oxygen vacancies rather than a polarity-induced potential build-up. This conclusion is supported by the observations that the critical thickness for inducing insulator-to-metal transition varies with GAO deposition conditions [11] and that annealing
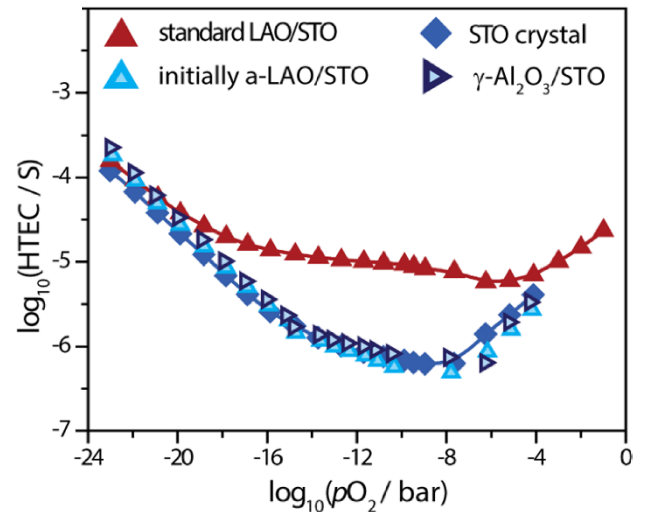
Figure 1: High temperature equilibrium conductance (HTEC) at 950 K as a function of the oxygen partial pressure, pO_2, for a SrTiO₃ (STO) substrate and STO with a high-temperature grown LaAlO₃ (LAO), room-temperature grown LAO (a-LAO) or γ-Al₂O₃ film. In all cases, the film thickness exceeds the critical thickness for inducing interface conductivity. Reprinted with permission from Ref. [6]. Copyright 2017, American Chemical Society.
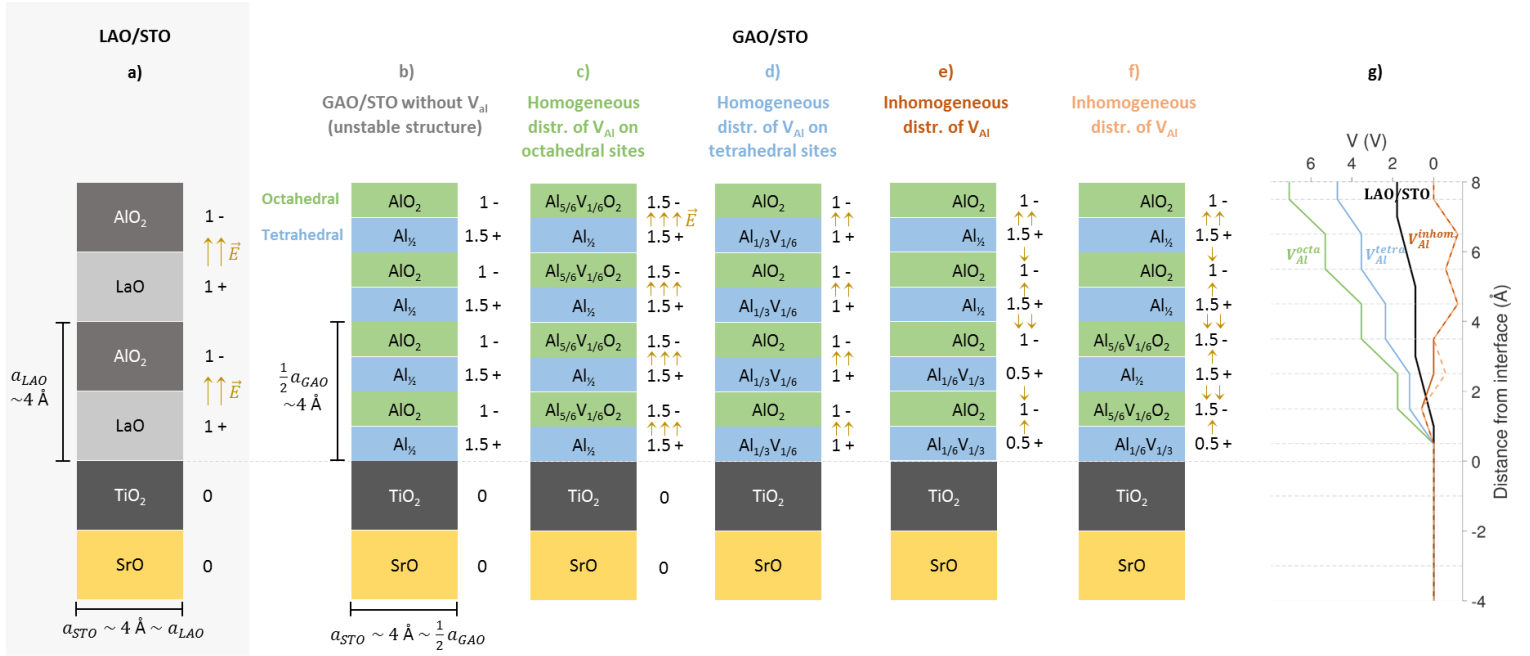
Figure 2. a-f) Schematics of the polarity of LAO/STO and GAO/STO viewed along the [001]-direction. For GAO/STO various distributions of aluminum vacancies (V) are considered. g) The resulting potential along the [001] direction for the different systems.

in oxygen at low temperatures (< 600 K) destroys the conductivity [12,13] with a characteristic activation energy consistent with oxygen vacancy movement in STO [13]. Here, we aim to explain this apparent paradox by revisiting the atomic structure of GAO. During the process, we identify a pathway that may turn GAO into a material with a tunable polarity.

2. Results and discussion: GAO has a cubic spinel crystal structure. In the general form (AB$_2$O$_4$), the cubic spinel unit cell is composed of 32 oxygen atoms, 16 B-site cations placed in an octahedral environment and 8 A-site cations in a tetrahedral environment (A$_8$B$_{16}$O$_{32}$). In the case of GAO, Al^{3+} occupies both A and B sites with a unit cell [14] of $a_{GAO} = 7.911$ Å. By virtue of compatible oxygen sublattices in STO and GAO, pseudo-epitaxial growth with $a_{GAO} \sim 2a_{STO}$ is possible [12]. The (001) planes of GAO can be viewed as alternating Al$_{\frac{1}{2}}$ and AlO$_2$ layers as depicted in Figure 2b. In order to obey charge neutrality each spinel unit cell contains on average 2⅔ aluminum vacancies (Al$_{21\frac{1}{3}}$O$_{32}$), which may be located on sites with octahedral or tetragonal symmetry. Consistent with ref. [10], a homogeneous distribution of aluminum vacancies exclusively on octahedral site gives layers with an alternating charge density of $\sigma = \pm 1\frac{1}{2} \, e/(\frac{1}{2}a_{GAO})^2$ (see Figure 2c). Assuming a relative dielectric constant of $\varepsilon_r = 9.5$ [4,15,16] we obtain a large potential build-up of 7.1 V/a_{GAO} (see Figure 2g). A homogeneous distribution on tetrahedral sites gives $\sigma = \pm 1 \, e/(\frac{1}{2}a_{GAO})^2$ and a reduced potential build-up of 4.8 V/a_{GAO} (see Figure 2d and g). In both cases, the potential build-up is significantly larger than that in LAO due to the lower dielectric constant of GAO. If the rapidly increasing potential in these cases was compensated by the electronic reconstruction, a critical thickness for forming a conducting interface would be expected to be less than one unit cell, taking into account the band alignment of STO and GAO [10]. Experimentally, however, the critical thickness is observed to be around 1.5 unit cells [12,17]. In terms of the polar classification, both distributions lead to a type 3 surface with a non-

zero dipole moment and, for a sufficiently thick film, require a substantial reconstruction to stabilize the surface [1]. An inhomogeneous distribution of aluminum vacancies can, however, lead to a very different polarity. There is some evidence for such an inhomogeneous distribution from X-ray studies [18] of single crystal GAO which find that Al is distributed over both octahedral and tetrahedral sites in a ratio 63:37. For a GAO thickness of one unit cell (8 atomic layers), Figure 2e and f depicts two distributions where GAO has no net dipole moment and no monotonously increasing potential. These atomic structures can be classified as type 2 [1]. Note that the distribution of Al between octahedral and tetrahedral sites in Figure 2f is 0.31, which compares favorably to distribution found in the X-ray study. The electrostatic potential of both solutions remains between -1.2 and 0.6 eV throughout the 8 atomic layers. This is significantly lower than the potential increase from 2.8 to 3.8 eV corresponding to the LAO thickness increase from 3 u.c. to 4 u.c. that causes conductivity in STO [5].

The general condition for non-polarity of a film with M atomic layers, the i'th layer having a charge density of σ_i, can be written as:

$$\sum_{i=1}^{M} (M - 2i + 1)\sigma_i = 0,$$

subject to the constraint of over-all charge neutrality, $\Sigma_i \sigma_i = 0$. For GAO, we introduce aluminum vacancies (V) in the Al$_{1/2}$ and AlO$_2$ layers, which can be described as alternating layers of Al$_{x_i}$V$_{1/2 - x_i}$ (i odd; charge $3x_i$) and Al$_{x_i}$V$_{1-x_i}$O$_2$ (i even; charge $3x_i - 4$). There are no non-polar solutions for fewer than 8 atomic layers (one unit cell). At a thickness of one unit cell, Figure 2e and f give two simple non-polar distributions. As the thickness increases, the number of different solutions increases rapidly. The configuration which actually will be realized, will be the kinetically accessible state with the lowest total energy. We will discuss the kinetics and energetics next:

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Chen et al [12] found that each RHEED oscillation detected during the growth of the film corresponds to growing a charge neutral block composed of two atomic layers as depicted in Figure 2 with a total thickness of ¼ unit cell (2 Å). The charge neutrality entails that each block initially is polar, and diffusion of aluminum vacancies between individual blocks is required to make GAO overall non-polar. The energy barrier for Al diffusion in GAO is lowered by the large number of intrinsic aluminum vacancies and may be as low as 0.6 eV [19]. In a typical pulsed laser deposition, thin GAO films (< 10 nm) are deposited at ~600 °C at low oxygen background pressures ($< 10^{-6}$ bar) where the plasma plume is freely expanding with plasma species arriving at the sample surface with kinetic energies exceeding 10 eV [20]. At such deposition conditions, aluminum is expected to be highly mobile across the entire GAO thickness. Even for films thick enough to hinder a sufficient aluminum diffusion throughout the entire film, GAO can be overall non-polar if diffusion over short distances results in repeating non-polar units such as the one in Figure 2e or f. The aluminum mobility, however, severely decreases if the deposition temperature is lowered or a less energetic deposition method is used.

Predicting the most thermodynamically stable aluminum vacancy distribution requires careful analysis well beyond the scope of this short communication. The total energy contains contributions from vacancy-vacancy interactions, coordination of vacancy positions (tetragonal vs. octahedral), symmetry breaking from the interface & GAO surface in addition to the energy contribution from the polarity. The high temperature equilibrium conductance measurements, however, directly probe the thermodynamically stable situation experimentally, and the lack of signature of sufficiently polar GAO films makes the non-polar aluminum vacancy contributions likely to be energetically favorable. This is further supported by (i) the lowering of the surface energy by conversion from a type 3 to 2 polarity [1], (ii) the lack of a polarity signature in the low-temperature annealing [12,13], (iii) the absence of energy shifts in aluminum core levels and the oxygen $2p$ valence state [10] and (iv) the dependence of the critical GAO thickness on the deposition conditions [11].

An intriguing consequence of this interpretation is that it may be possible to change the polarity by applying electric fields. Considering, e.g., the case with one unit cell GAO presented in Figure 2e and f, the non-polar solutions are found by locating aluminum vacancies close to STO. If a positive top-gate potential is applied relative to the grounded electron gas at the interface, electromigration of aluminum vacancies towards the GAO surface yield a polar GAO film. In this way, the GAO film may effectively act as a ferroelectric material. The possibility for electromigration at room or slightly elevated temperatures seems likely in the view of frequently reported room temperature electromigration of oxygen vacancies with a similar energy barrier [21,22].

3. Conclusion: In conclusion, we have presented a possible solution for the apparent paradox in which experiments show a lack of the distinguishing features of the polar discontinuity at the GAO/STO interface although GAO is generally considered to be polar. We show that inhomogeneous distributions of aluminum vacancies highly affect the polarity and allow for non-polar GAO films for certain thicknesses. Thus, we have presented a possible resolution of the paradox. However, it should be noted that alternative explanations may also be possible, such as defect formations, and we encourage future studies to clarify the actual structure of the GAO film on STO. In particular, density-functional based calculations will be useful for assessing the relative stability of the configurations considered here.

References:

[1]   P.W. Tasker, The stability of ionic crystal surfaces, J. Phys. C Solid State Phys. 12 (1979) 4977.

[2]   N. Nakagawa, H.Y. Hwang, D.A. Muller, Why some interfaces cannot be sharp, Nat. Mater. 5 (2006) 204–209. doi:10.1038/nmat1569.

[3]   L. Yu, A. Zunger, A polarity-induced defect mechanism for conductivity and magnetism at polar–nonpolar oxide interfaces, Nat. Commun. 5 (2014) 5118. doi:10.1038/ncomms6118.

[4]   J. Krupka, R.G. Geyer, M. Kuhn, J.H. Hinken, Dielectric Properties of Single Crystals of Al2O3, LaAl03, NdGaO3, SrTiO3, and MgO at Cryogenic Temperatures, IEEE Trans. Microw. Theory Tech. 42 (1994) 1886.

[5]   S. Thiel, G. Hammerl, A. Schmehl, C.W. Schneider, J. Mannhart, Tunable quasi-two-dimensional electron gases in oxide heterostructures, Science. 313 (2006) 1942–1945. doi:10.1126/science.1131091.

[6]   Z.Q. Liu, C.J. Li, W.M. Lü, X.H. Huang, Z. Huang, S.W. Zeng, X.P. Qiu, L.S. Huang, A. Annadi, J.S. Chen, J.M.D. Coey, T. Venkatesan, Ariando, Origin of the Two-Dimensional Electron Gas at LaAlO3/SrTiO3 Interfaces: The Role of Oxygen Vacancies and Electronic Reconstruction, Phys. Rev. X. 3 (2013) 021010. doi:10.1103/PhysRevX.3.021010.

[7]   P. Moetakef, T.A. Cain, D.G. Ouellette, J.Y. Zhang, D.O. Klenov, A. Janotti, C.G. Van de Walle, S. Rajan, S.J. Allen, S. Stemmer, Electrostatic carrier doping of GdTiO 3 /SrTiO 3 interfaces, Appl. Phys. Lett. 99 (2011) 232116. doi:10.1063/1.3669402.

[8]   Z. Popović, S. Satpathy, R. Martin, Origin of the Two-Dimensional Electron Gas Carrier Density at the LaAlO3 on SrTiO3 Interface, Phys. Rev. Lett. 101 (2008) 256801. doi:10.1103/PhysRevLett.101.256801.

[9]   F. Gunkel, S. Hoffmann-Eifert, R.A. Heinen, D.V. Christensen, Y.Z. Chen, N. Pryds, R. Waser, R. Dittmann, Thermodynamic Ground States of Complex Oxide Heterointerfaces, ACS Appl. Mater. Interfaces. 9 (2017) 1086–1092. doi:10.1021/acsami.6b12706.

[10]   P. Schütz, F. Pfaff, P. Scheiderer, Y.Z. Chen, N. Pryds, M. Gorgoi, M. Sing, R. Claessen, Band bending and alignment at the spinel/perovskite γ−Al2O3/SrTiO3 heterointerface, Phys. Rev. B. 91 (2015) 165118. doi:10.1103/PhysRevB.91.165118.

[11]   Y.Z. Chen, N. Bovet, T. Kasama, W.W. Gao, S. Yazdi, C. Ma, N. Pryds, S. Linderoth, Room Temperature Formation of High-Mobility Two-Dimensional Electron Gases at Crystalline Complex Oxide Interfaces, Adv. Mater. (2013) 1.

[12]   Y.Z. Chen, N. Bovet, F. Trier, D.V. Christensen, F.M. Qu, N.H. Andersen, T. Kasama, W. Zhang, R. Giraud, J. Dufouleur, T.S. Jespersen, J.R. Sun, A. Smith, J. Nygård, L. Lu, B. Büchner, B.G. Shen, S. Linderoth, N. Pryds, A high-mobility two-dimensional electron gas at the spinel/perovskite interface of γ-Al2O3/SrTiO3, Nat. Commun. 4 (2013) 1371. doi:10.1038/ncomms2394.

[13]   D.V. Christensen, von S. et al Merlin, Controlling the Carrier Density of SrTiO3–based Heterostructures with Annealing, Submitt. Adv Electr Mat. (2017).

[14] R.-S. zhou, R.L. Snyder, Structures and Transformation Mechanisms of the η, γ and θ Transition Aluminas, Acta Crystallogr. B47 (1991) 617–630.

[15] S. Guha, E. Cartier, N.A. Bojarczuk, J. Bruley, L. Gignac, J. Karasinski, High-quality aluminum oxide gate dielectrics by ultra-high-vacuum reactive atomic-beam deposition, J. Appl. Phys. 90 (2001) 512–514. doi:10.1063/1.1373695.

[16] X. He, Z.-X. Tang, B. Zhang, Y. Wu, A new deembedding method in permittivity measurement of ferroelectric thin film material, Prog. Electromagn. Res. Lett. 3 (2008) 1–8.

[17] D.V. Christensen, F. Trier, M. von Soosten, G.E.D.K. Prawiroatmodjo, T.S. Jespersen, Y.Z. Chen, N. Pryds, Electric field control of the γ-Al$_2$O$_3$/SrTiO$_3$ interface conductivity at room temperature, Appl. Phys. Lett. 109 (2016) 021602. doi:10.1063/1.4955490.

[18] Ľ. Smrčok, V. Langer, J. Křesťan, γ-Alumina: a single-crystal X-ray diffraction study, Acta Crystallogr. C. 62 (2006) i83–i84. doi:10.1107/S0108270106026850.

[19] S.T. Murphy, B.P. Uberuaga, J.B. Ball, A.R. Cleave, K.E. Sickafus, R. Smith, R.W. Grimes, Cation diffusion in magnesium aluminate spinel, Solid State Ion. 180 (2009) 1–8. doi:10.1016/j.ssi.2008.10.013.

[20] A. Sambri, D.V. Christensen, F. Trier, Y.Z. Chen, S. Amoruso, N. Pryds, R. Bruzzese, X. Wang, Plasma plume effects on the conductivity of amorphous-LaAlO$_3$/SrTiO$_3$ interfaces grown by pulsed laser deposition in O$_2$ and Ar, Appl. Phys. Lett. 100 (2012) 231605. doi:10.1063/1.4727905.

[21] R. Waser, M. Aono, Nanoionics-based resistive switching memories, Nat. Mater. 6 (2007) 833–840.

[22] K. Szot, W. Speier, G. Bihlmayer, R. Waser, Switching the electrical resistance of individual dislocations in single-crystalline SrTiO$_3$, Nat. Mater. 5 (2006) 312–320. doi:10.1038/nmat1614.