Polarity-induced oxygen vacancies at LaAlO₃/SrTiO₃ interfaces

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Using first-principles density-functional-theory calculations, we find a strong position and thickness dependence of the formation energy of oxygen vacancies in LaAlO₃│SrTiO₃ (LAO│STO) multilayers and interpret this with an analytical capacitor model. Oxygen vacancies are preferentially formed at p-type SrO│AlO₂ rather than at n-type LaO│TiO₂ interfaces; the excess electrons introduced by the oxygen vacancies reduce their energy by moving to the n-type interface. This asymmetric behavior makes an important contribution to the conducting (insulating) nature of n-type (p-type) interfaces while providing a natural explanation for the failure to detect evidence for the polar catastrophe in the form of core level shifts.

I. INTRODUCTION

Extremely high carrier mobilities have recently been observed when interfaces consisting of LaO and TiO₂ layers are formed between insulating LaAlO₃ (LAO) and SrTiO₃ (STO) perovskites.[1] Even though the physical origin of this metallic behavior is still under debate,[2–8] most experimental[9–20] and theoretical[21–30] studies have reached a consensus that the so-called *polarity discontinuity* between these materials plays a crucial role; in the absence of any relaxation mechanism, alternate stacking of positively (LaO⁺) and negatively (AlO₂⁻) charged layers on the nonpolar STO substrate would give rise to a huge effective internal electric field, leading to a divergence of the electrostatic potential with increasing thickness of LAO. Reflecting general developments in the field of polar oxides,[31] three mechanisms have been suggested to avoid this instability: charge transfer,[2] atomic relaxation,[13,20–24] or the creation of oxygen vacancies[4,5] and other defects.[8,14]

The first mechanism refers[2] to the transfer of electrons from a surface AlO₂ layer to the interface TiO₂ layer by the internal electric field. The excess charge at the interface balances the polar discontinuity and leads to conducting behavior of the interface. This mechanism is strongly supported by the observation of an insulator-metal transition induced by either an external electric field or by increasing the thickness of the LaAlO₃ layer.[10] However, direct experimental evidence of charge transfer, in the form of core level shifts, has not yet been found.[6,7] The insulating behavior of the p-type interface[1] is also not readily accommodated in this picture.

The second mechanism, atomic relaxation in the presence of the internal electric field, that is analogous to the buckling of Ti-O-Ti chains in an external field in SrTiO₃, has been discussed by a number of authors.[13,20–24] It can eliminate the diverging potential by introducing a compensating electric field. A third way to resolve the polar instability is to introduce defects at interfaces. Oxygen vacancies (and other defects) created during the growth of LAO on STO are invoked by Herranz *et al.*[4] and Kalabukhov *et al.*[5] to understand the high mobility carriers. The long relaxation time of the electric-field-induced insulator-metal transition[16] suggests the possibility of interface defect diffusion.

While the first two mechanisms have received much theoretical attention,[21–28] the relationship between the creation of defects and polarity has not been clarified theoretically. To demonstrate the coupling of polarity and oxygen vacancy formation and throw some light on the interplay with atomic relaxation and charge transfer, we calculate from first principles the formation energy of oxygen vacancies in LAO│STO multilayers as a function of their location in the multilayer.

II. METHOD

We focus on (m,m) LAO│STO multilayers containing m layers each of LAO and STO with alternating p- and n-type interfaces. Because samples are grown on STO substrates, we fix the in-plane lattice constant at the calculated equilibrium value of STO and calculate the LAO out-of-plane lattice constant by minimizing the total energy of strained bulk LAO. Oxygen vacancies are modeled in a 2×2 lateral supercell and for each vacancy position all atoms are allowed to relax with the volume of the structure fixed. Most of the results reported below were obtained with the 159 atom $2 \times 2 \times (4,4)$ supercell depicted in Fig. 1 containing a p and an n interface. The periodically repeated single-oxygen vacancy in a layer consisting of 2×2 unit cells should be compared to the ∼25% oxygen vacancy concentration in a layer suggested by experiment.[2] The local density approximation (LDA) calculations were carried out with the projector augmented wave method[32] as implemented in the Vienna *ab initio* simulation package (VASP).[33] A kinetic energy cutoff of 500 eV was used and the Brillouin zone of the 159 atom supercell was sampled with an $8 \times 8 \times 2$ k-point grid in combination with the tetrahedron method. Inclusion of correlation effects (LDA+U) would modify the electrostatic potential profile slightly but not change our main conclusion which is dominated by the polarity of the system.

In thermodynamic equilibrium, the concentration of oxygen vacancies is determined by the free energy for vacancy formation, $\Omega^{\mathrm{Vac}} = E_{\mathrm{SC}}^{\mathrm{Vac}} - E_{\mathrm{SC}} + \mu_{\mathrm{O}}(T,p_{\mathrm{O}_2})$.[34,35] The energies E can be calculated from first principles and in the present case where we use periodic supercells, $E_{\mathrm{SC}}^{\mathrm{Vac}}$ and E_{SC} are the energies of supercells with and without an oxygen vacancy.
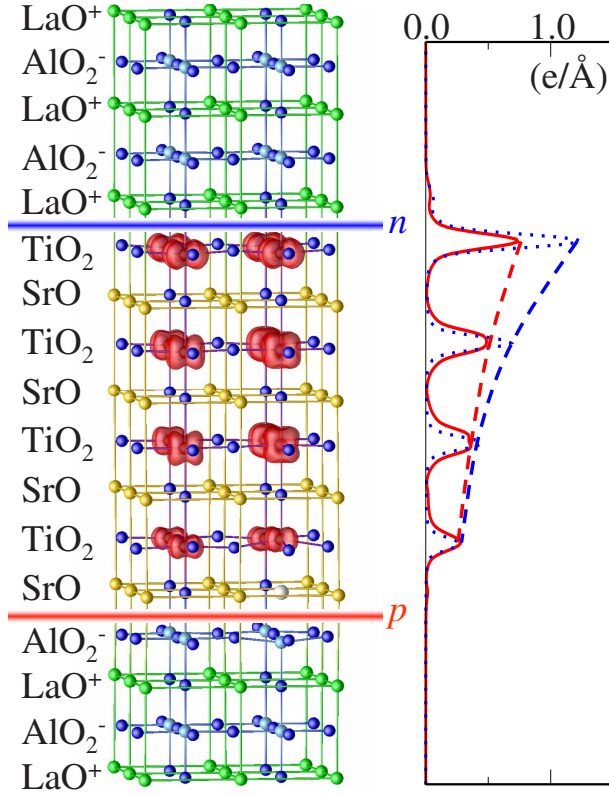
FIG. 1. (Color online) Left panel: the unit cell of a $2 \times 2 \times (4+4)$ LAO|STO multilayer with an oxygen vacancy at the p-type interface. Dark (blue) spheres represent oxygen atoms and the oxygen vacancy is marked by a white sphere. Charge density isosurfaces corresponding to a value of 0.015 $e/\text{Å}^3$ for occupied states in the conduction bands are colored red. Right panel: plane-averaged charge density as a function of z for oxygen vacancies at p- (full line/red) or n- (dotted line/blue) type interfaces.

$\mu_O(T, p_{O_2})$ is the chemical potential of oxygen that depends on the temperature T and oxygen pressure p_{O_2} during growth or annealing. Unfortunately, there is no reliable way of determining the absolute value of μ_O during LAO thin film growth by pulsed laser deposition. However, thin films of STO grown on STO substrates under the same experimental conditions as LAO thin films on STO can be used as a reference system to study oxygen vacancies.[4,5,36] In this paper we define the formation energy of an oxygen vacancy in an LAO|STO multilayer with respect to that in bulk STO, $\Delta\Omega^{\text{Vac}} = \Omega^{\text{Vac}}_{\text{LAO}|\text{STO}} - \Omega^{\text{Vac}}_{\text{STO}}$. If we assume that the oxygen chemical potential μ_O for LAO thin film growth is the same as that during growth of STO thin films under the same experimental conditions, then the oxygen chemical potentials μ_O cancel in the expression for $\Delta\Omega^{\text{Vac}}$ that then describes oxygen vacancy formation induced by LAO with reference to STO. It is worth noting that though $E^{\text{Vac}}_{\text{STO}}$ converges only slowly with the size of supercell,[37] this does not alter the conclusions we will draw. $\Delta\Omega^{\text{Vac}}$ will be seen to span a range of ± 1.0 eV as a result of polarity and this range is much larger than the uncertainty in $E^{\text{Vac}}_{\text{STO}}$ which is converged to ± 0.09 eV.
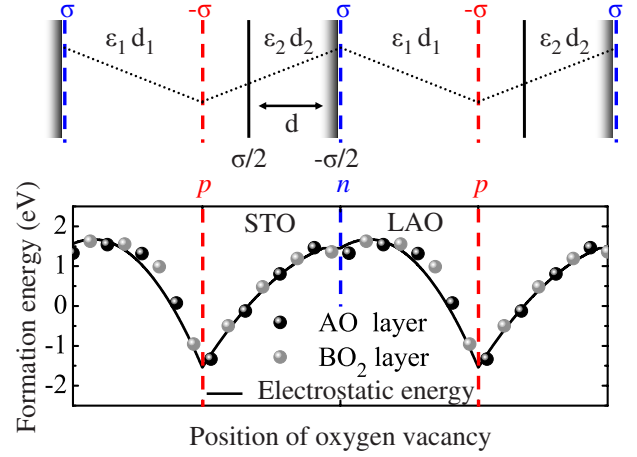

FIG. 2. (Color online) Position dependence of the formation energy of an oxygen vacancy in a $2 \times 2 \times (4+4)$ LAO|STO multilayer calculated from first principles without relaxation (symbols) and using an analytical capacitor model (solid line). n and p interfaces are indicated by vertical (blue and red) dashed lines. A schematic of the capacitor model is shown in the upper panel. The electrostatic potential profile for the vacancy-free structure is shown as a dotted line. The vertical black line at a distance d from the n interface represents the oxygen vacancy layer. Two excess electrons are transferred to the TiO_2 layer at the n interface (shaded gray line).

III. RESULTS

We begin by calculating $\Delta\Omega^{\text{Vac}}(z)$ as a function of the position (z) of an oxygen vacancy without atomic relaxation. The most striking feature of the results shown in the lower panel of Fig. 2 is the asymmetry for forming a vacancy at the n and p interfaces. $\Delta\Omega^{\text{Vac}}$ is lowest when the oxygen vacancy is at the p interface, highest close to the n interface and is nonlinear in z. It spans a range of about 3 eV between the two interfaces and differs in the LAO and STO layers. We can capture the essential behavior of $\Delta\Omega^{\text{Vac}}(z)$ in terms of a modified parallel-plate capacitor model.

A. Model

The average electrostatic potential of defect-free LAO|STO multilayers, as probed by the energy levels of core states in LDA calculations, exhibits a simple symmetric triangular form as if the n and p interfaces were positively and negatively charged with charge density $\pm\sigma = \mp e/a^2$, where a is the lattice constant of bulk STO. As sketched in the top panel of Fig. 2, the plates of the capacitor are separated by a thickness d_1 (d_2) of insulating LAO (STO) with dielectric constants ε_1 (ε_2) determined by the electronic polarization only in the absence of ionic relaxation. Such a model was recently used to describe the evolution of the dielectric properties of LAO|STO multilayers with increasing layer thickness resulting in an insulator-metal transition.[27] Based on this simple capacitor model, the estimated internal electric fields are huge, $\frac{1}{\varepsilon} 1.2 \times 10^{11}$ V/m or ~ 0.9 V/unit cell in LAO, and the electrostatic potential (dotted line in Fig. 2) diverges with increasing thickness of LAO.
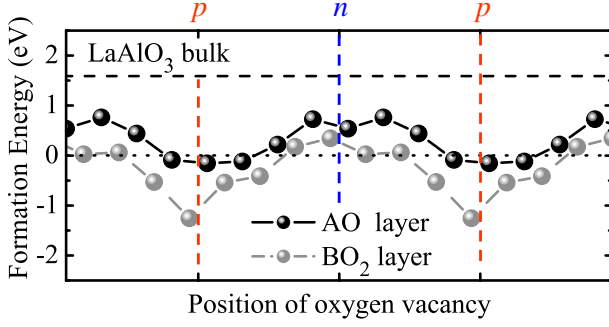
FIG. 3. (Color online) Position dependence of the formation energy of an oxygen vacancy in a $2 \times 2 \times (4+4)$ LAO|STO multilayer relative to that of a vacancy in bulk STO (horizontal dotted line) calculated from first principles with relaxation. Black and gray symbols are for vacancies in AO and BO_2 layers, respectively. The formation energy of an oxygen vacancy in bulk LAO is shown as a dashed horizontal line.

We extend this model to encompass the layer of vacancies constructed in our supercell approach. Because oxygen is divalent, removal of a neutral oxygen atom in a bulk insulating material such as LAO or STO leaves two excess electrons in the conduction band weakly bound to the oxygen vacancy. In an LAO|STO multilayer, the potential energy of the electrons in the internal electric field far exceeds this binding energy and the total energy can be reduced by moving the two electrons to the conduction band minimum at the n interface leaving a sheet of positive charge at the oxygen vacancy plane a distance d away. Assuming that the excess electrons are on Ti ions at the TiO_2|LaO interface, independent of where the oxygen vacancies were formed, we can calculate the d dependent change in the electrostatic energy to be $\frac{\sigma^2/\varepsilon_0}{d_1\varepsilon_2+d_2\varepsilon_1}\{-d_1+\frac{\varepsilon_1}{\varepsilon_2}(d_2-d)\}d$. It comprises two parts: the energy to insert a sheet of positive charge density $\sigma/2$ in the LAO|STO capacitor background, $-\frac{2\sigma^2/\varepsilon_0}{d_1\varepsilon_2+d_2\varepsilon_1}d_1d$, and the potential energy of the positively and negatively charged sheets $\frac{\sigma^2/\varepsilon_0}{d_1\varepsilon_2+d_2\varepsilon_1}\{d_1+\frac{\varepsilon_1}{\varepsilon_2}(d_2-d)\}d$. The calculated LDA core level shifts of ~ 0.9 V/unit cell can be used to estimate $\varepsilon_1+\varepsilon_2$ ~ 52 leaving one free parameter in the model, the ratio $\varepsilon_2/\varepsilon_1$. Taking this to be 1.5 results in the solid curve in Fig. 2. The good fit of this simple model makes it clear that the internal fields induced by the polar layered structure can lower the formation energy of oxygen vacancies at the p interface very substantially and that the origin of the asymmetry between LAO and STO (the lack of reflection symmetry in the vertical dashed lines in Fig. 2) is the difference in their dielectric constants. The residual interaction between the field-ionized oxygen vacancies and electrons accounts for the nonlinear behavior of the formation energy.

Atomic relaxation can be expected to strongly suppress the polarity. Nevertheless, when our structures are fully relaxed, some essential features of $\Delta\Omega^{Vac}(z)$ are unchanged, see Fig. 3. In particular, the formation energy has a minimum at the p interface and a maximum close to the n interface while the minimum formation energy is more than 1 eV lower than in bulk STO. Including atomic relaxation differentiates between vacancy formation in AO and BO_2 layers;
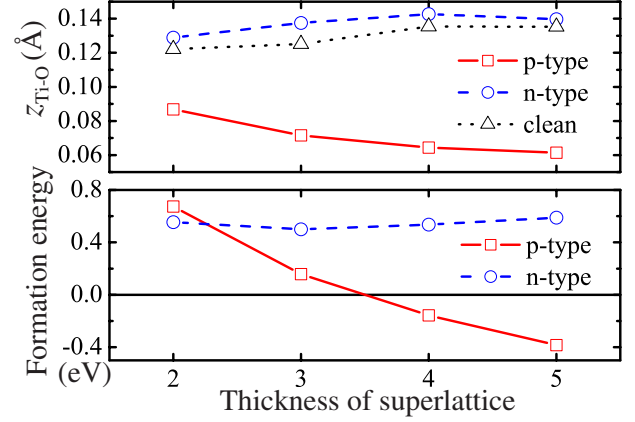

FIG. 4. (Color online) Upper panel: projection of the Ti-O-Ti separation along the z direction due to buckling for clean interfaces ($\triangle$) and when vacancies are formed at the p ($\square$) and at the n ($\bigcirc$) interface. Lower panel: formation energy of an oxygen vacancy as a function of the multilayer thickness for p and n interfaces in a $2 \times 2 \times (m+m)$ LAO|STO multilayer with relaxed structure.

the latter are energetically more favorable though the behavior as a function of z is essentially the same. The lower formation energy in BO_2 layers can be understood in terms of the types of relaxations possible within the constraints imposed by stacking the different layers in a multilayer. To simplify the discussion, we focus on the *less* favorable case of oxygen vacancies in AO layers so that our conclusions will also be applicable for BO_2-layer vacancies.

B. Critical thickness

For a capacitor with fixed charge density σ, the electric field is constant and the electrostatic potential increases as the plate separation (LAO thickness) is increased, a feature that is supported by both experimental[10,16] and theoretical[21–24,27] studies. Because of its dependence on the electrostatic potential, we expect the formation energy of oxygen vacancies to depend on the multilayer thickness. Since the minimum and maximum formation energies occur at or close to the p and n interfaces, respectively, we focus on these formation energies. We further assume equal thicknesses m of the STO and LAO layers and plot $\Delta\Omega^{Vac}$ as a function of m in Fig. 4. At the n interface it is almost constant in value and ~ 0.6 eV higher than for bulk STO. At the p interface however, it decreases with increasing m and becomes negative for a critical value of m between 3 and 4. Thus, for $m \geq 4$ oxygen vacancies are preferentially formed at p interfaces rather than in the bulk of the materials or at the n interface. The existence of a critical thickness is evidence for "uncompensated polarity" in thin LAO.[38]

For an ideal LAO|STO multilayer without oxygen vacancies, the *zigzag* buckling of Ti-O-Ti and Al-O-Al chains will act to quench the internal electric field.[13,21–24,27] Since oxygen vacancies at a p-type interface accompanied by charge transfer can strongly suppress polarity, they should also suppress Ti-O ferroelectric type buckling. Figure 4 shows that this is indeed the case. Oxygen vacancies at a p-interface suppress the buckling strongly while vacancies at an n inter-

face do not. The core level shifts, which represent the internal electric field, are reduced from 0.9 to 0.15 V/unit cell. In this sense, oxygen-vacancy formation, charge transfer, and atomic relaxation act together in response to polar catastrophe.

A single-oxygen vacancy donates two electrons to the system and the distribution and character of these excess electrons will dominate its transport properties. In a clean LAO│STO multilayer, the electrostatic potential at the p interface is lower than at the n interface so even if oxygen vacancies are generated at the p interface, the excess electrons will be driven by the electrostatic potential to the n interface. The charge distribution of the occupied conduction band states is plotted in Fig. 1. Consistent with previous studies,[18,25] these have Ti d_{xy}-orbital character if the Ti ions are close to the interface, otherwise they consist of a mixture of Ti d_{xz}- and d_{yz}-orbital characters. Though the introduction of oxygen vacancies represents a major change to the atomic structure, the change to the electronic structure is minor compared to a clean LAO│STO multilayer with only n-type interfaces.

IV. DISCUSSION

Even though it is energetically favorable to form oxygen vacancies at a p interface, the excess electrons are transferred to the n interface which will tend to be conducting while the p interfaces will be insulating. This asymmetry implies a spatial separation between impurity scattering and transport regions which, by analogy with proximity doping in semiconductor heterostructures, can give rise to a high mobility at LAO│STO interfaces. This result agrees with recent experimental data[2] which shows evidence for the presence of oxygen vacancies at the p interface while the mobile carriers are at the n interface.

The formation of oxygen vacancies can be suppressed by applying high oxygen pressures either during growth or in a post-growth anneal step. To confirm that polarity could induce oxygen vacancies at LAO│STO interfaces grown under high oxygen pressures of order 10^{-3} mbar, we need to relate the calculated $\Delta\Omega^{Vac}$ to thin film or multilayer growth conditions in a more practical way. As discussed in Sec. II, the oxygen vacancy formation energy Ω^{Vac} depends on the oxygen chemical potential $\mu_O(T, p_{O_2})$ during growth or annealing. Even though the absolute value of μ_O is unknown, its dependence on temperature and pressure is reasonably described by $1/2 \ kTln(p_{O_2})$.[35] This tells us how raising the oxygen pressure increases the oxygen chemical potential and suppresses the formation of oxygen vacancies. For example, STO thin films grown on an STO substrate at oxygen pressure above 10^{-6} mbar are insulating while below 10^{-6} mbar they are conducting.[5,36] If we associate the conductivity with doping by oxygen vacancies, this implies that 10^{-6} mbar is a threshold pressure for oxygen vacancy formation in STO thin

films at which the formation energy becomes small enough to account for a measurable concentration of carriers. The smaller this threshold energy is, the closer $\mu_O(p_{O_2} = 10^{-6}$ mbar) approaches $E_{STO} - E_{STO}^{Vac}$. Assuming the oxygen chemical potential for growth of LAO and STO thin films on STO is the same under comparable experimental conditions, we find $\Delta\Omega^{Vac} = \Omega^{Vac}(p_{O_2} = 10^{-6}$ mbar) which implies that our calculated $\Delta\Omega^{Vac}$ actually represents the energy to form oxygen vacancies at LAO│STO interfaces grown at an oxygen pressure of 10^{-6} mbar. When the oxygen pressure is increased from 10^{-6} to 10^{-3} mbar, the increase in oxygen chemical potential and Ω^{Vac} is only ~ 0.3 eV which is still relatively small and only sufficient to compensate the polarity-induced reduction in vacancy formation energy at p-type interfaces when the LAO layer is very thin. Thus we argue that for LAO│STO interfaces grown or annealed at typical high oxygen pressures, the formation of oxygen vacancies induced by polarity of LAO cannot be excluded.

Though most experimental studies have been made[1,2,10] on samples consisting of STO substrates covered with several layers of LAO which only contain a single n interface, the conclusions of this paper about the position and thickness dependence of the formation energy of oxygen vacancies should be qualitatively applicable to the single interface case if we regard the surface of LAO as a pseudo-p-type interface.[30] Several experiments suggest[8,14] the possibility of cation intermixing at interfaces. We calculated the energy cost of Sr-La interface mixing and found it to be energetically favorable at n interfaces. This implies that n interfaces should be rougher than p interfaces.[2]

V. CONCLUSION

Using first-principles calculations, we show how oxygen-vacancy formation, charge transfer, and atomic relaxation in response to polar discontinuity at LAO│STO interfaces are strongly coupled. Oxygen vacancies are preferentially formed at p rather than n interfaces and the thickness-dependent formation energy provides an alternative explanation for the critical thickness observed in experiments while simultaneously explaining the failure to observe core level shifts. The conduction electrons produced when an oxygen vacancy is formed at a p interface move to the n interface where their interaction with the vacancies is minimal explaining the observed high mobilities.

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