Inevitable high density of oxygen vacancies on the surface of LaAlO$_3$/SrTiO$_3$ heterostructures

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Using density-functional-theory (DFT) calculations with the HSE06 hybrid functional, we accurately evaluate the critical thickness of LaAlO$_3$ film for the intrinsic doping in LaAlO$_3$/SrTiO$_3$ (LAO/STO) heterostructures. The calculated critical thickness of 6 unit-cell (uc) layers suggests to rule out the intrinsic doping mechanism. We also calculate the density of oxygen vacancies on the LAO surface at varying LAO thicknesses, preparation oxygen pressures and temperatures by using the condition of chemical equilibrium and DFT calculations. We find that once LAO thickness $\geq$3 uc high-density ($\sim 10^{14}$ cm$^{-2}$) oxygen vacancies will inevitably exist on the LAO surface of the LAO/STO heterostructures even though the samples are grown under high oxygen pressure. The oxygen vacancies are stabilized by releasing the electrostatic energy in the LAO film.

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Perovskite transition metal oxides have rich functionalities and have been a hotspot in the area of material science. In recent years, heterostructures of complex perovskite oxides made this area more colorful and appealing. Some intriguing properties, which are absent in the individual components, may emerge in the heterostructures. The polar-nonpolar heterostructure LAO/STO is a typical example. LAO and STO are both wide-gap band insulators, but a high-mobility two-dimensional electron gas (2DEG) was found to exist at the LAO/STO interface. Moreover, ferromagnetism, superconductivity, metal-to-insulator transition (MIT) were successively found at the interface. These properties closely rely on the interfacial carriers. The polarity of the LAO film plays a key role in the formation of the carriers.

In defect-free LAO/STO heterostructures, a polar electric field will appear in the LAO film along [001] direction. With increasing LAO thickness the electrostatic energy accumulated in the LAO film will increase accordingly, finally leading to the electronic reconstruction as proposed by Nakagawa et al., i.e., charge transfers from the LAO surface into the interface at the STO side. Based on this picture two mainstream doping mechanisms, i.e. intrinsic doping and oxygen-vacancy doping, were proposed. As shown in Figs. 1(a) and (b), both doping mechanisms are triggered by the polar field in the LAO film. Usually, it was believed that the intrinsic doping occur in the LAO/STO heterostructures prepared under high oxygen pressures because high oxygen pressure could easily release oxygen vacancies in oxides. Several DFT calculations showed that in defect-free LAO/STO there is a striking band gap in the LAO film and a critical LAO thickness of 4 uc layers for the intrinsic doping, at which the valence band maximum (VBM) of the LAO surface exceeds the conduction band minimum (CBM) of the STO. Meanwhile, several experiments also reported that the LAO/STO heterostructures prepared under high oxygen pressures present a critical thickness of 4 uc for conducting interface, seemingly conforming the intrinsic doping. However, the expected large band gradient, as the necessary and direct evidence of intrinsic doping, has not yet been observed, in contrast, the observed values are negligible. Moreover, increasing experimental studies have shown that for the LAO/STO heterostructures prepared under high oxygen pressures even at the LAO thickness of 3 uc layers the localized carriers already appear at the interface. Noticeably, the above DFT studies, which performed the calculations with Local-density-approximation (LDA) or generalized-gradient-approximation (GGA) functional, largely underestimated the band gap of STO ($\sim 1.8$ eV in the calculations, while 3.2 eV in experiment). This implies that the calculations underestimated the critical thickness of the intrinsic doping. Thus, the intrinsic doping is doubtable. On the other hand, theoretical studies on oxygen vacancies showed that oxygen vacancies may easily exist on the surface of LAO/STO heterostructures because the charge transfer from the LAO surface to the interface could release the electrostatic energy accumulated in the LAO film.

Nowadays, the polar-nopolar heterostructures like LAO/STO have been extensively used to tune the electronic properties of perovskite oxides. However, the doping mechanism in LAO/STO heterostructures is still uncertain. In this paper, we study the intrinsic and oxygen-vacancy doping mechanisms in LAO/STO heterostructures. First, we accurately calculate the critical thickness of LAO film for the intrinsic doping by using density-functional-theory (DFT) calculations with the HSE06 hybrid functional. The calculated value of 6 uc implies that the intrinsic doping mechanism is ruled out. Then, we derive the density of oxygen vacancies on the LAO surface at varying LAO thickness, preparation oxygen pressures and temperatures by using the condition of chemical equilibrium and DFT calculations. We find that once LAO thickness $\geq$3 uc high-density ($\sim 10^{14}$ cm$^{-2}$) oxygen vacancies will inevitably exist on the LAO surface of the LAO/STO heterostructures.

To correctly evaluate the critical LAO thickness for intrinsic doping in the defect-free LAO/STO heterostructures, we carried out DFT calculations with the HSE06 hybrid functional by using VASP code. The HSE06 hybrid functional, which contains 23% of the exact exchange and 77% of the PBE exchange energy, correctly estimates the band gap of bulk STO (3.2 eV). The heterostructures were modeled in $c(2\times2)$ supercells, which consist of 4 uc layers of STO, n (n=4, 5, 6) uc layers of LAO and about 14 Å of vacuum region. The atoms in the bottom two STO layers were fixed at their bulk
positions and the others were fully relaxed until the forces on atoms were less than 0.02 eV/Å. The dipole correction method was used to correct the spurious electrostatic field induced by the periodic boundary condition and the potential differencebetween two different terminations of the slabs.23

FIG. 1. Band diagrams of (a) intrinsic doping and (b) surface oxygen-vacancy doping in the LAO/STO heterostructures.

![Band diagrams](image1)

of 4 uc observed in experiments. And considering the observed negligible band-shifts in the LAO layers, we suggest that the intrinsic doping mechanism is basically ruled out.

Usually, oxygen vacancies hardly exist in bulk LAO under a high oxygen pressure condition because the binding energy of an oxygen atom in LAO bulk (∼11 eV) is far higher than in oxygen gas (∼5 eV). In contrast to bulk LAO, oxygen vacancies could easily form on the LAO surface of the LAO/STO heterostructures because the transfer of oxygen-vacancies induced charge from the LAO surface into the interface could partially compensate the polar field, therefore lowering the electrostatic energy as shown in Fig. 1(b). The energy gain arising from lowering the electrostatic energy compensates the binding-energy cost of the surface oxygen vacancies. Previous DFT studies have shown that the formation energy of an oxygen vacancy on the surface of the LAO/STO heterostructures could be a few eV lower than in bulk LAO, and oxygen vacancies favor to appear on the surface of the LAO/STO heterostructures.24,25

A quantitative relation between the density of surface oxygen vacancies and the LAO thickness, oxygen pressure, temperature can be established by using the chemical equilibrium condition. For grown LAO/STO heterostructures in chamber with the oxygen pressure $P$ and temperature $T$, under chemical equilibrium the chemical potential of the surface oxygen atoms on the surface of the heterostructures $\mu_{\text{surf}}$ is equal to the chemical potential of oxygen atoms in the oxygen gas $\mu_{\text{gas}}$. Using the method in Ref. 33 $\mu_{\text{gas}}$ can be expressed as

$$\mu_{\text{gas}}(T, p) = \frac{1}{2} [E_{O_2} + \mu_{O_2}(T, p^0) + k_B T \ln(P/P^0)],$$

where $E_{O_2}$ is the binding energy of a gaseous oxygen molecule, $\mu_{O_2}(T, p^0)$ is relative chemical potential of gaseous oxygen molecules at the standard pressure $P^0=1$ bar and temperature $T$, $E_{O_2}$ was obtained from the first-principles calculation, and $\mu_{O_2}(T, p^0)$ was obtained by following the method in Ref. 33. Figure 3(a) displays $\mu_{\text{gas}}$, in which the ranges of oxygen pressure and temperature used in previous experiments are covered. $\mu_{\text{gas}}$ can vary from -7.1 eV (at low pressure and high temperature) to -5.4 eV (at high pressure and low temperature).

For a LAO/STO heterostructure with $N_{OV}$ oxygen vacancies on the surface, $\mu_{\text{surf}}$ can be written in the form (see Supplementary information)

$$\mu_{\text{surf}} = \frac{\partial (E_0 - E_{OV})}{\partial N_{OV}} + 3k_B T + T \frac{\partial S}{\partial N_{OV}}.$$  

The chemical potential is contributed by three parts, the changes of total energy, thermal vibration energy, and entropy’s term, which are denoted as $\mu_{\text{surf}}^{\text{en}}, \mu_{\text{surf}}^{\text{te}},$ and $\mu_{\text{surf}}^{\text{tv}},$ respectively. $\mu_{\text{surf}}^{\text{en}}$ can be approximately derived as $\mu_{\text{surf}}^{\text{en}} = k_B T \ln(n_0 - n_{OV})/(n_{OV})$, where $n_0$ is area density of oxygen atoms on the surface AlO$_2$ layer and $n_{OV}$ is area density of the oxygen vacancies. To derive $\mu_{\text{surf}}^{\text{te}}$ we resort to a capacitor model combined with DFT calculations. The total energy is decomposed into two parts, the binding energy of oxygen atoms on the surface of LAO film without the polar field and
the electrostatic energy induced by the polar field in the LAO film. Considering that the LAO film with the surface and interface is a parallel-plate capacitor with thickness \(d\) and area \(A\), and the oxygen vacancies discharge the capacitor, so the total energy difference can be expressed as

\[
E_0 - E_{OV} = \frac{d}{2 \epsilon_0 \epsilon_r A} [Q_0^2 - (Q_0 - 2eN_{OV})^2] - N_{OV} E_b
\]

where \(\epsilon_r\) is the relative dielectric constant of the LAO film, \(E_b\) is the binding energy of an oxygen atom at the LAO surface without the polar field, \(Q_0\) is the total polar charge on the surface without oxygen vacancy, the factor of \(-2e\) before \(N_{OV}\) means that one oxygen vacancy discharges the capacitor by a charge of two electrons. Thus,

\[
\mu_{surf}^e = -E_0 - \frac{d e^2}{2 \epsilon_0 \epsilon_r} (8n_{OV} - 4n_0),
\]

where \(n_0\) (\(n_0^e = Q_0/A\)) is the density of polar charge at the surface, i.e. \(0.5e\) per uc area. First-principles calculations with supercell method can give the total energies of supercells without oxygen vacancy and with various densities of oxygen vacancies. By fitting the formula \(E_0 - E_{OV}\) we could extract the two parameters, \(E_b\) and \(\epsilon_r\), and then obtain the chemical potential \(\mu_{surf}\) as function of the LAO thickness and density of oxygen vacancies. The total-energy calculations were carried out with the VASP code (see detailed method and calculated data in Supplementary information). Four densities of oxygen vacancies, one vacancy in \((2 \times 2\), \((3 \times 2\), \((3 \times 3\), and \((4 \times 3\) supercells respectively, were calculated.

Figure 3b) displays \(\mu_{surf}\), which increases remarkably with increasing LAO thickness except in the vicinity of the high end of the density of oxygen vacancies. Figure 3c) shows the increment of electrostatic energy by adding one oxygen atom to fill up a surface oxygen vacancy, i.e., the electrostatic energy released by an oxygen vacancy. In the region of low density of oxygen vacancies the energy increases largely with increasing LAO thickness because the thick LAO film accumulates more electrostatic energy than the thin film. While in the vicinity of the high end of the density of oxygen vacancies the energies for different thicknesses converge to zero because the polar filed has been compensated and more oxygen vacancies do not release electrostatic energy any more. Comparing with \(\mu_{gas}\) (-7 - 5 eV), \(\mu_{surf}\) in a large region of the density of oxygen vacancies is higher, indicating that surface oxygen vacancies will definitely exist in the heterostructures with thicker LAO film.

Using the relation \(\mu_{gas} = \mu_{surf}\) under the condition of chemical equilibrium we derive the density of oxygen-vacancy-induced carriers at the LAO/STO interface and plot it in Fig. 4. For all LAO thickness the carrier densities decrease with increasing the oxygen pressure or decreasing the temperature. For \(d = 1, 2\) uc the carrier densities change sensitively with varying the oxygen pressure and temperature, and the carrier densities could be negligible at high pressure and low temperature. In contrast, for \(d \geq 3\) uc the carrier densities change slowly with the oxygen pressure and temperature, and keep high values \((2 \times 10^{13} - 2.2 \times 10^{14} cm^{-2})\) even under a very high pressure (\(>1\) bar). This result evidently shows that for the LAO/STO with over 3 uc layers of LAO a high density of oxygen vacancies about \(10^{14} cm^{-2}\) inevitably exist at the LAO surface even through a high oxygen pressure is applied to sample preparation. Noticeably, with increasing LAO thickness the density of carriers will saturate at 6 uc because according to the intrinsic doping picture the electrostatic energy in the defect-free LAO film will reach to the maximum. And the maximum carrier density in the LAO/STO heterostructures grown under high oxygen pressures could not reach to the value of 0.5 electron per uc area, i.e. \(3.3 \times 10^{13} cm^{-2}\). As shown in Fig. 4c), the surface
oxygen vacancies on the LAO surface are mainly stabilized by releasing the electrostatic energy. Whereas at this carrier density $\mu_{\text{surf}} (\sim 10 \text{ eV})$ is far lower than $\mu_{\text{surf}}$, implying that oxygen atoms will flow into LAO to fill up the vacancies.

Noticeably, under high oxygen pressure and low temperature the carrier densities for $d = 1$, 2 uc and $d \geq 3$ uc present a remarkable difference. In the former the carrier density could be negligible or very low, while in the later high-density carriers always exist. Moreover, the cation intermixing, which was observed to exist in 2 uc layers at the interface could further reduce the polar field in the LAO film and might lower the the carrier density of $d = 1$, 2 uc to an undetectable level. This is in very good agreement with recent experimental results obtained by using resonant inelastic soft x-ray scattering, in which no interfacial carrier was observed until 3 uc layer of LAO. Several previous experimental studies also presented the same evidence. It should be noted that the carriers observed in the LAO/STO with 3 uc layers of LAO are localized and has no contribution to conduction. In addition, since the high-density carriers induced by the surface oxygen vacancies compensate the main part of the polar field, the band gradient in the LAO film should be quit small. This is consistent with the small band gradient observed in the experiments.

In conclusion, our hybrid-functional DFT calculations clearly show that in defect-free LAO/STO heterostructures the intrinsic doping occurs at the LAO thickness of 6 uc layers, instead of 4 uc layers. This indicates that the observed metal-insulator transition at 4 uc LAO layers is not induced by the intrinsic doping. On the contrary, our theoretical study on the density of oxygen vacancies show that the intrinsic doping never happened, instead oxygen vacancies on the LAO surface produce the carriers because the oxygen vacancies are stabilized by releasing the electrostatic energy in the LAO film. Once LAO thickness $\geq 3$ uc layers, a high density of oxygen vacancies inevitably appears on the surface even through the heterostructure is prepared under a very high oxygen pressure. Accordingly, a high density of carriers is generated at the interface, and it varies dominantly with the LAO thickness, and slowly with oxygen pressure and temperature.

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I. SUPPLEMENTARY INFORMATION

For a LAO/STO heterostructure with $N_{OV}$ oxygen vacancies on the surface, the Gibbs free energy $G_{OV}$ is

$$G_{OV} = U_{OV} - TS = G_0 + (U_{OV} - U_0) - TS$$

$$= G_0 + (E_{OV} - E_0) - 3k_BT N_{OV} - TS,$$

where $U_{OV}$ and $U_0$ are the internal energies of the LAO/STO heterostructure with oxygen vacancies and without oxygen vacancies, respectively, $S$ is the configuration entropy of oxygen vacancies and it is zero for the LAO/STO heterostructure without oxygen vacancy, $G_0$ is the Gibbs free energy of the heterostructures without oxygen vacancy and it is equal to $U_0$. The internal energy $U_{OV}$ or $U_0$ comprises of two parts, the total energy at zero temperature $E_{OV}$ or $E_0$ and the thermal vibration energy. The item $-3k_BT N_{OV}$ is the difference of thermal vibration energy between the heterostructure without oxygen vacancy and with $N_{OV}$ oxygen vacancies. The $\mu_{surf}$ follows from

$$\mu_{surf} = -\frac{\partial G_{OV}}{\partial N_{OV}} = \frac{\partial (E_0 - E_{OV})}{\partial N_{OV}} + 3k_BT + T \frac{\partial S}{\partial N_{OV}}.$$

The configuration entropy of the oxygen vacancies can be evaluated approximately as

$$S = k_B \ln W = k_B \ln \frac{N_O!}{(N_O - N_{OV})! N_{OV}!},$$

where $N_O$ is the total number of oxygen sites at vacancy-free surface $\text{AlO}_2$ layer.

The total-energy calculations were carried out with the VASP code. The generalized gradient approximation for the exchange-correlation functional was applied to evaluated the electron-electron interaction. The calculations were performed with the projector augmented wave method, in which the cutoff kinetic energy for the plane wave basis set is 450 eV. The LAO/STO heterostructures were modeled in $(2 \times 2)$, $(3 \times 2)$, $(3 \times 3)$, and $(4 \times 3)$ supercells. The total energies of the supercells without oxygen vacancy and with an oxygen vacancy on the LAO surface were calculated. The supercells consist of 4 uc layers of STO, n (n=1,2,3) uc layers of LAO and about 14 Å of vacuum region. The atoms in the bottom two STO layers were fixed at their bulk positions and the others were fully relaxed until the forces on the atoms were less than 0.02 eV/Å. The dipole correction was used to correct the spurious electrostatic field induced by the periodic boundary condition and the potential difference between two terminations of the slabs.

Table I lists the total energy differences $E_{OV} - E_0$. By fitting with the formula of $E_0 - E_{OV}$ we derived the $E_b$ and $\epsilon_r$, thus we obtained $\mu_{surf}^\text{tot}$ for $d = 1, 2, 3$ uc. As mentioned
TABLE I. $E_{OV} - E_0$ (eV) for the LAO/STO heterostructures with various LAO thicknesses $d$ (uc), in which $E_0$ and $E_{OV}$ are the total energies of the LAO/STO supercell without oxygen vacancy and with one oxygen vacancy at the LAO surface, respectively. $E_b$ is the binding energy of an oxygen atom on the LAO surface without the polar field.

| Supercell | (2×2) | (3×2) | (3×3) | (4×3) |  $E_b$ (eV) |
|-----------|-------|-------|-------|-------|-------------|
| $d = 1$   | 8.975 | 8.874 | 8.660 | 8.347 | 9.900       |
| $d = 2$   | 8.525 | 8.227 | 7.952 | 7.515 | 9.981       |
| $d = 3$   | 7.699 | 7.263 | 6.788 | 6.237 | 9.856       |

above, in the calculations with HSE06 functional the intrinsic doping does not occur in the LAO/STO until 6 uc layers of LAO, therefore our model is also validate for the LAO/STO with the 4 and 5 uc LAO. We decomposed the 3 uc layers of LAO into an interface uc layer, a middle uc layer and a surface uc layer, and derived their dielectric constants respectively. We consider that the LAO films of 4 and 5 uc layers just have one and two more middle uc layers compared with the film of 3 uc layers, and the binding energy $E_b$ for the 4 and 5 uc is the same as that for 3 uc. By this means we derived the $\mu_{\text{surf}}^\text{exf}$ for the LAO/STO heterostructures with $d = 1, 2, 3, 4, 5$ uc layers of LAO.