PHYSICAL REVIEW B **82**, 125412 (2010)

Origin of insulating behavior of the *p*-type $LaAlO_3/SrTiO_3$ interface: Polarization-induced asymmetric distribution of oxygen vacancies

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(Received 29 April 2010; revised manuscript received 15 July 2010; published 9 September 2010)

It is revealed from first-principles calculations that polarization-induced asymmetric distribution of oxygen vacancies plays an important role in the insulating behavior at *p*-type $LaAlO_3/SrTiO_3$ interface. The formation energy of the oxygen vacancy (V_O) is much smaller than that at the surface of the $LaAlO_3$ overlayer, causing all the carriers to be compensated by the spontaneously formed V_O's at the interface. In contrast, at an *n*-type interface, the formation energy of V_O is much higher than that at the surface, and the V_O's formed at the surface enhance the carrier density at the interface. This explains the puzzling behavior of why the *p*-type interface is always insulating but the *n*-type interface can be conducting.

DOI: 10.1103/PhysRevB.82.125412 PACS number(s): 68.35.Dv, 61.72.jd, 71.15.Nc, 73.20.−r

I. INTRODUCTION

Recently, it has been shown that the conductivity at the interfaces between two band insulators such as polar $LaAlO_3$ and nonpolar $SrTiO_3$ can be vastly different, depending mostly on the type of interface and the thickness of the overlayer.[1–7] In the case of an overlayer of $LaAlO_3$ grown on $SrTiO_3$ along the [001] direction, it is found that by controlling the termination of the substrate $SrTiO_3$ (001) surface, two kinds of abrupt interfaces can be formed. One is the electron-rich *n*-type LaO/TiO_2 interface, and the other is the electron-poor *p*-type AlO_2/SrO interface. Experimental measurements reveal that the *n*-type interface can be metallic and conducting, and the *p*-type interface is always insulating. This unusual behavior has attracted much attention; several models have been proposed that attempt to understand the phenomena.[8–18] The conductivity of the *n*-type interface is usually explained within the picture of polarization catastrophe.[1,9] In this picture, two-dimensional (2D) electron gas near the LaO/TiO_2 interface is formed to counteract the dipolar electric field that arises from the alternating stacking of the $(LaO)^+$ and $(AlO_2)^-$ planes in the $LaAlO_3$ overlayer. The accumulated 2D electron gas near the interface, therefore, is responsible for the *n*-type conductivity. However, the origin of the insulating *p*-type interface has not been fully understood.

Experimental studies have shown that oxygen vacancy (V_O) plays an important role in the measured conductivity of both types of interfaces. It is claimed that under growth condition of low oxygen pressure, the V_O's formed at the $SrTiO_3$ substrate during the growth contribute to the unusually high density of carriers at the *n*-type interface.[12] For the *p*-type interface, the compensating V_O's at the interface have been proposed to account for the absence of free carriers.[13] On the theory side, for the ideal *p*-type interface, first-principles calculations show that the mobilities of the holes are much lower than their counterpart electrons in the *n*-type interface and are strongly anisotropic.[18] Strong correlation effects of O_{2p} states are also proposed to account for the observed insulating behavior in addition to the charge compensation of V_O's at the *p*-type interface.[19] However, the microscopic picture of the V_O-induced effects has not been fully described.[20] What remains unclear is the trend of the stability of V_O in the polarized $LaAlO_3$ overlayer and how the formation of V_O's depends on the growth condition and polarity of the overlayer. To completely understand the conductivity of the $LaAlO_3/SrTiO_3$ interfaces, it is crucial to address these questions and especially to justify the origin of the insulating *p*-type interface.

In $SrTiO_3$, the nominal charge states of Sr and Ti are 2+ and 4+, respectively, so the two (001) surfaces (SrO and TiO_2 terminated) are both neutral. On the other hand, in $LaAlO_3$, the nominal charge states of La and Al are both 3 + so the LaO-terminated (001) surface has 0.5 extra electrons and the AlO_2-terminated surface has 0.5 extra holes for each 1×1 surface cell. In Fig. 1, the atomic structures for the two kinds of stoichiometric interfaces are shown. If the interface is formed between SrO and AlO_2 surfaces as shown in Fig. 1(a), it has extra holes so it is called a *p*-type interface. In this case, the surface of the $LaAlO_3$ overlayer is LaO-terminated, thus it is *n*-type. If the interface is formed between TiO_2 and LaO surfaces as shown in Fig. 1(b), it has extra electrons and is therefore *n*-type. In this case, the surface of the $LaAlO_3$ overlayer is AlO_2 terminated, thus is *p*-type.

In this paper, using first-principles calculations, we calculate the formation energy of the V_O in the polarized $LaAlO_3$ overlayer that forms the interfaces with the $SrTiO_3$ (001) substrate. It is revealed that due to the polarization effect, the formation energy of V_O changes monotonically across the $LaAlO_3$ overlayer. For the *p*-type interface, the formation energy of V_O at the interface side is much smaller than the one at the *n*-type surface side. Under the oxygen-poor growth condition, the V_O formation energy at the interface can be so small that the V_O can form spontaneously and compensate all the holes at the interface, making the interface insulating. For the *n*-type interface, the situation is exactly opposite. The formation energy of V_O at the *n*-type

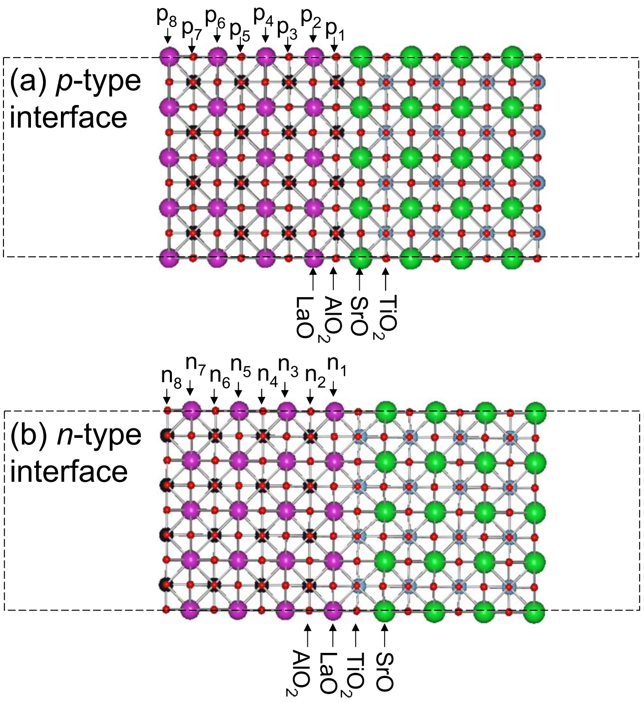

FIG. 1. (Color online) The supercells of (a) the *p*-type and (b) the *n*-type interfaces of $LaAlO_3/SrTiO_3$ used in the calculations.

interface is much larger than that at the *p*-type surface, and the holes at the surface will be compensated by the formation of V_O's. This will only enhance the carrier density and thus the conductivity of the *n*-type interface. This explains why the *p*-type interface is always insulating while the *n*-type can be conducting for the $LaAlO_3/SrTiO_3$ interfaces.

II. COMPUTATIONAL METHOD

The calculations are based on the density-functional theory as implemented in the VASP code.[21] We use the projector-augmented wave method with Perdew-Burke-Ernzerhof (PBE) exchange-correlation potentials.[22] The calculated lattice constants of perovskite $SrTiO_3$ and $LaAlO_3$ are 3.94 and 3.85 Å, which are within 1% of the experimental values of 3.905 and 3.865 Å. To calculate the formation energy of V_O, we use supercells containing slabs with eight 4×4 bilayers separated by a vacuum region of more than 10 Å along the normal of the interface (Fig. 1). The cut-off energy used for the plane-wave basis set is 400 eV, and the integration in the Brillouin zone is done only at the Γ point. All the atoms are relaxed until the forces are less than 0.02 eV/Å. The dipole corrections are calculated and included in the total energies.

The formation energy of a single V_O in the neutral polarized $LaAlO_3$ overlayer is given by

$$E_f = E_{total} - E_{host} + \mu_O, \tag{1}$$

where E_{total} is the calculated total energy of the supercell with one V_O; E_{host} is the total energy of the host, i.e., the supercell without V_O; and μ_O is the chemical potential of the oxygen reservoir.

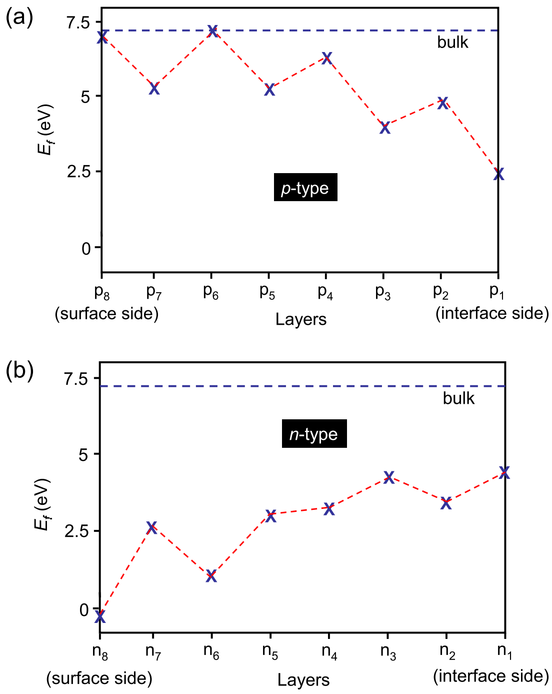

FIG. 2. (Color online) The formation energies [Eq. (1)] of oxygen vacancies in the $LaAlO_3$ overlayer for (a) *p*-type and (b) *n*-type interfaces at the oxygen-rich (O_2) growth condition. The designations of the layers correspond to those in Fig. 1. The dashed lines indicate the formation energy in the bulk.

III. RESULTS AND DISCUSSIONS

We calculate the formation energies of V_O located in each of the layers designated by p_1-p_8 for the *p*-type interface and n_1-n_8 for the *n*-type interface, respectively, in the $LaAlO_3$ overlayer as shown in Fig. 1. The calculated values are shown in Fig. 2 where the μ_O is set to $1/2\ \mu(O_2)$, i.e., at O-rich limit. We should note that the variation in V_O formation energy at various positions is independent of the oxygen chemical potential. We see that for both *p*-type and *n*-type interfaces, the formation energies oscillate between LaO and AlO_2 layers, and are relatively larger at the positively charged $(LaO)^+$ layer. This is because V_O behaves as a positively charged donor in the system, and, due to the Coulomb repulsion between the V_O donor and the $(LaO)^+$ layer, the formation energy of V_O is larger at the LaO layers. Besides the oscillation, we find (i) the formation energies decrease monotonically from the *n*-type side (either surface or interface) to the *p*-type side of the overlayer for both types of interfaces. For the *p*-type AlO_2/SrO interface, the formation energy reaches the maximum at the *n*-type LaO surface of the $LaAlO_3$ overlayer, close to the value in the bulk [Fig. 2(a)]. For the *n*-type LaO/TiO_2 interface, the formation energy is the largest at the interface. (ii) The formation energy at the *p*-type surface [Fig. 2(b)] is lower than that at the *p*-type interface [Fig. 2(a)]. (iii) Figure 3(a) shows the dependence of the formation energy on the thickness of the $LaAlO_3$ overlayer for V_O at the *p*-type AlO_2 surface of the overlayer with an *n*-type LaO/TiO_2 interface. It is shown that the thicker the overlayer, the lower the formation energy.

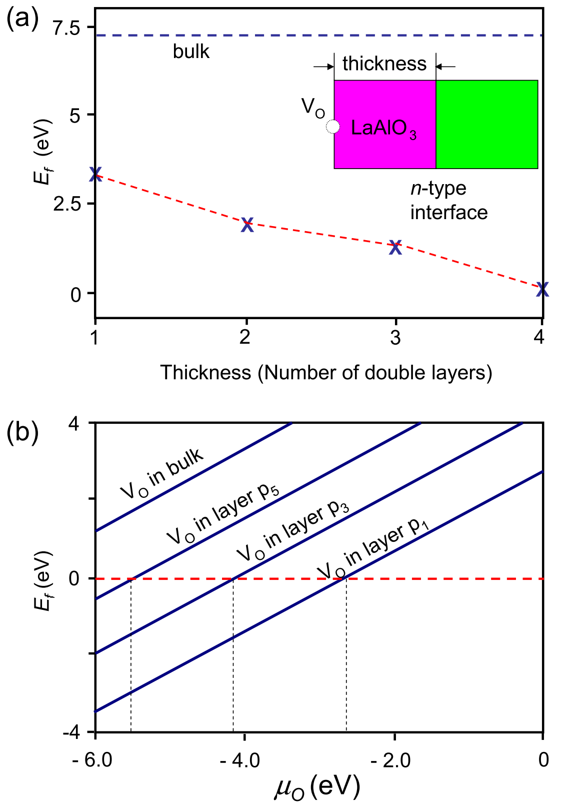

FIG. 3. (Color online) (a) The dependence of the formation energy of V_O on the thickness of the LaAlO$_3$ overlayer for the *n*-type interface. For the *p*-type interface, a similar trend is expected. (b) Formation energies as a function of μ_O for V_O in p$_1$, p$_3$, and p$_5$ layers with the *p*-type interface.

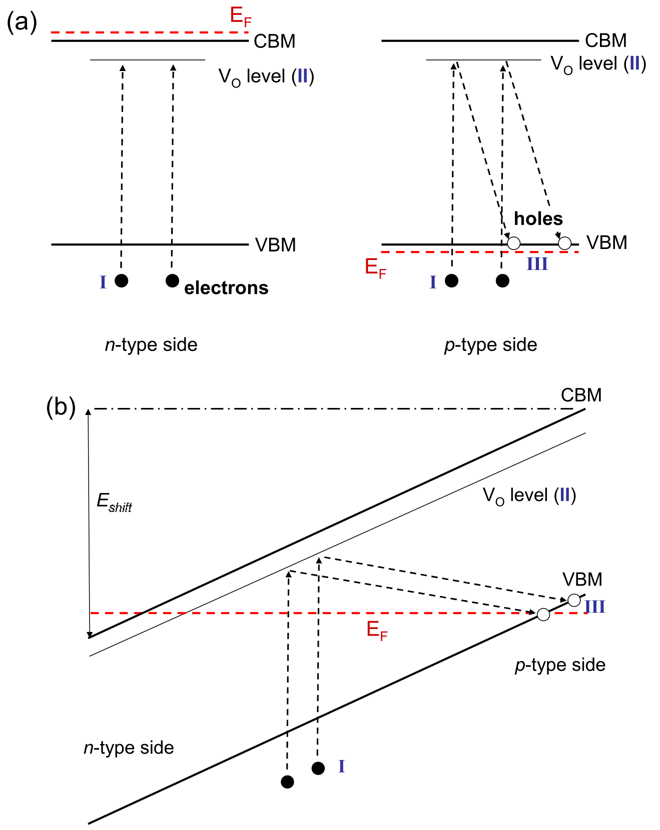

FIG. 4. (Color online) (a) Schematics showing the electron processes during the formation of V_O at (left) *n*-type and (*p*-type) surface or interface of the polarized LaAlO$_3$ overlayer. (b) Schematic showing the electron process when the vacancy site is away from the *p*-type surface or interface. The energy shift (E_{shift}) is because of the polarization of the overlayer.

(iv) The results presented in Figs. 2 and 3(a) are for O-rich growth condition. The absolute values of the formation energies, however, can be much smaller under the O-poor condition. Because of the large calculated formation energy of −18.0 eV for LaAlO$_3$, the achievable O chemical potential μ_O at La- and Al-rich conditions can be as low as −6.0 eV before LaAlO$_3$ dissociates. In Fig. 3(b), we show the formation energies (E_f) as a function of μ_O for V_O located at p$_1$, p$_3$, and p$_5$ layers for the *p*-type interface. For better comparison, the bulk values are also shown in the same figure. From Fig. 3(b), we can see that for V_O in layer p$_1$, the formation energy can be negative if μ_O is lower than a critical value of −2.6 eV. For V_O located at p$_3$ and p$_5$ layers, the critical μ_O's are −4.1 eV and −5.5 eV, respectively. This indicates that at the *p*-type interface the V_O can be spontaneously formed during the growth if μ_O is low enough, i.e., under the oxygen-poor growth condition.

To understand the general trends described above, we investigated the band structures and defect energy levels of the calculated systems. (i) The reason that the formation energy of V_O is low at the *p*-type surface or interface side (Fig. 2) can be easily understood by the fact that the formation of each V_O creates two electrons located close to the conduction-band minimum (CBM), as schematically shown in Fig. 4(a). At the *p*-type side, these electrons will compensate the extra holes near the valence-band maximum, and thus will gain energy. The charge transfer also results in a Coulomb attraction between the V_O donor and host, further lowering the formation energy. When the V_O moves away from the *p*-type surface or interface because of the existence of the dipole electric field in this polar crystal, the energy gain by charge transfer is reduced due to the reduced energy level difference. The Coulomb coupling is also reduced due to the increased separation between electrons and holes [Fig. 4(b)]. This explains the monotonic behavior of the formation energy in both cases. (ii) The band gap at the *p*-type LaAlO$_3$ surface is larger than in the interface; moreover, creating defects at the surface breaks fewer bonds than in the bulk. Taken together, this explains why the formation energy of V_O at the *p*-type surface is less than that at the *p*-type interface (Fig. 2). (iii) Due to the interaction between the surface and interface, the number of hole states at the *p*-type surface depends on the layer thickness; it increases when the layer thickness increases and approaches its maximum value at 0.5 hole per 1×1 surface cell.[18] This explains why the formation energy of V_O decreases when the LaAlO$_3$ overlayer thickness increases [Fig. 3(a)]. This also suggests that when the 2D density of V_O is $0.25/1\times1$, all the holes on a perfect *p*-type surface or interface can be completely compensated.

The formation energy of V_O at the *p*-type surface or interface also depends on the 2D density of the formed V_O. This can be easily seen from Fig. 4(a), which shows that the favorability of V_O formation at the *p*-type surface or interface comes from the hole compensation. As the formation of V_O's at the *p*-type surface or interface continues, fewer holes are available. Therefore the formation energy of V_O will be closer to that in the bulk or at the *n*-type surface or interface.

From the above analysis, we can see that under experimental growth condition with low oxygen pressure, the formation energy of V_O at the *p*-type $LaAlO_3/SrTiO_3$ interface can be low enough to make V_O form spontaneously. The concentration of the formed V_O can reach a level at which all the extra holes at the interface are fully compensated. Thus there will be no free carriers at the *p*-type interface. This, in addition to the poor hole-transport properties associated with oxides,[18] explains why the *p*-type interface is always insulating. On the other hand, for the *n*-type interface, the formation of V_O takes place mostly on the polarized *p*-type surface. This will reduce the polarization of the $LaAlO_3$ overlayer, thus increasing the carrier density and enhancing the conductivity at the *n*-type interface.

It has been shown experimentally that there exists a critical thickness of four unit cells for the $LaAlO_3$ overlayer, above which the *n*-type interface starts conducting. The origin of the critical thickness can be explained simply by the charge transfer from the *n*-type surface to the *p*-type surface of the polarized overlayer and the resulted potential shift across the overlayer. The formation of V_O at the *p*-type surface enhances the charge transfer so the critical thickness may show a slight decrease upon the spontaneous formation of V_O's.

We also examined the V_O formation on the $SrTiO_3$ side for the *p*-type interface. We found that the formation energy of V_O is also lowered compared with that in the $SrTiO_3$ bulk. So the density of V_O at $SrTiO_3$ side of the interface will also be higher than in the $SrTiO_3$ bulk. But, because the CBM of $SrTiO_3$ is about 2 eV lower than $LaAlO_3$, the formation-energy decrease in the $SrTiO_3$ side is not as dramatic as in the $LaAlO_3$ side. Therefore, most of the spontaneously formed V_O's would appear in the $LaAlO_3$ side of the interface.

IV. CONCLUSION

In conclusion, we show through first-principles calculations that in the $LaAlO_3/SrTiO_3$ interface, due to the polarization effect, an oxygen vacancy forms easily at the *p*-type interface, therefore, the carriers (holes) can be compensated easily by the spontaneous formation of V_O's. In addition to the poor hole-transport properties associated with oxides, this mechanism explains the puzzling behavior of the *p*-type $LaAlO_3/SrTiO_3$ interface being insulating while the *n*-type can be conducting. This mechanism is quite general and can be applied to tune electrical properties of other oxide interfaces for new functional applications.

ACKNOWLEDGMENTS

The work is supported by the start-up grant to Lixin Zhang from Nankai University in P. R. China. The work at NREL is supported by the U.S. DOE under Contract No. DE-AC36-08GO28308.

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