Modulation of electron carrier density at the n-type LaAlO$_3$/SrTiO$_3$ interface by water adsorption

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Abstract

We investigate the energetic stability and dissociation dynamics of water adsorption at the LaAlO$_3$ surface of the n-type LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface and its effect on the electronic properties of the interface by carrying out first-principles electronic structure calculations. In an ambient atmosphere at room temperature the configuration of 1 monolayer (ML) of water molecules including $3/4$ ML of dissociated water molecules adsorbed at the surface is found to be most stable, whereas the configuration of 1 ML of dissociated water molecules is metastable. Water molecule dissociation induces an up-shift of the valence band maximum (VBM) of the LAO surface, reducing the gap between the VBM of the LAO surface and the conduction band minimum of the STO. For the LAO/STO interface with three LAO unit-cell layers, once the coverage of dissociated water molecules reaches $1/2$ ML the gap is closed, the interface becomes metallic and the carrier density at the LAO/STO interface increases with increasing coverage of dissociated water molecules. Our findings suggest two ways to control the conductivity at the LAO/STO interface: (I) an insulator–metal transition by adsorbing an amount of water at the bare surface; (II) a carrier density change by the transition between the most stable and the metastable adsorption configurations for 1 ML coverage in an ambient atmosphere at room temperature.

(Some figures may appear in colour only in the online journal)

1. Introduction

The behavior of a two-dimensional electron gas (2DEG) at interfaces has been one of the most intriguing subjects of electronic material research. Because of its versatile and remarkable properties it has drawn much attention from both fundamental research and application studies. One of the key findings in this subject is that a 2DEG can be generated at the interface between two insulating metal oxides, LaAlO$_3$/SrTiO$_3$ (LAO/STO) [1]. At the n-type LAO/STO interface between (LaO)$^+$ and (TiO$_2$)$^0$ layers, a high density (a few $10^{13}$ cm$^{-2}$) and high mobility ($\sim 10^3$ cm$^2$ V$^{-1}$ s$^{-1}$) electron gas has been realized at low temperature [1]. In addition, ferromagnetism [2] and superconductivity [3] were also reported at the same interface.

As LAO and STO are two band insulators, finding the electron gas at their interface immediately triggered extensive research to reveal the formation mechanism of the electron gas. So far, two mechanisms have been proposed and well accepted. One is the polar catastrophe, in which the polar electric field in the LAO film shifts up the valence band maximum (VBM) of the LAO film layer by layer and finally leads to a charge transfer from the valence band of the LAO surface layer to the conduction band of the STO [4]. It was found in Thiel et al’s experiment and confirmed theoretically that there is a critical thickness of the LAO film (4 unit cells) below which the interface is insulating and above which the interface becomes metallic [5–7]. The other mechanism is the role of oxygen vacancies, which were explicitly demonstrated in experiments to exist at the STO side for samples grown at
low oxygen pressures [8, 9]. A theoretical study showed that oxygen vacancies also readily form at the LAO surface and produce a carrier charge with a density of no more than half an electron per unit cell (u.c.) area at the interface [10].

Recently, Cen et al reported a novel method to generate an electron gas at the LAO/STO interface [11, 12]. In their experiment, nanoscale control of the so-called insulator-to-metal transition (IMT) at the LAO/STO interface was realized by an atomic force microscope (AFM) tip scanning the LAO surface. A nanoscale conducting line can be formed at the interface by the AFM tip with a positive bias voltage writing on the LAO surface and the conducting line can be erased by the AFM tip with a negative bias voltage cutting the line. It is noticeable that this IMT happens only to the interface with three u.c. layers of LAO. Subsequent experimental studies suggested that this IMT may be related to water adsorption at the LAO interface [13, 14]. To interpret this phenomenon several assumptions have been proposed. Bi et al assumed that the adsorbed water is dissociated and the AFM tip with a positive bias voltage removes the hydroxyls (OH–) from the surface, as a result the remaining hydrogen atoms dope electron carriers at the interface [13]. However, first-principles electronic structure calculations have showed that, regardless of the LAO thickness, hydrogen adsorption on the LAO surface always induces a metallic interface [15], implying that the change at the LAO surface induced by the AFM tip scanning is not like Bi et al’s scenario. Xie et al speculated that water molecules are adsorbed at the LAO surface by a dipole–dipole interaction (the dipole of the water molecule and the dipole of the LAO film) [14], i.e., two hydrogen atoms of a water molecule approach the LAO surface and the oxygen atom points to the outside. This will lead to an enhanced polarity of the LAO film with adsorbed water compared to the bare LAO film, probably resulting in a charge transfer from the surface to the interface. However, many studies have shown that water adsorption on oxide surfaces is via the formation of a chemical bond between the oxygen atom of the water molecule and the metal atom at the oxide surfaces [16–24] instead of a dipole–dipole interaction, basically ruling out Xie et al’s scenario. This is because that the energy gain of the chemical adsorption on oxide surfaces, 1–3 eV per water molecule [17, 21, 22, 24], is far larger than that of the physical adsorption, about 0.2 eV per molecule [25]. So far, although this nanoscale control of the transport property at the LAO/STO interface has presented a very promising application on nanoscale memory device, the so-called ‘atomic force pencil and eraser’ [26], its physical nature is still a puzzle.

In this paper we present a first-principles study of the electronic and structural characteristics of water molecules adsorbed at the LAO surface of the n-type LAO/STO interface, including surface atomic structures, thermodynamic stabilities, dissociation processes of water molecules, and electronic properties. We find that in an ambient atmosphere at room temperature the adsorption configuration of one monolayer (ML) of water molecules including 3/4 ML of dissociated water molecules is most stable, while the configuration of 1 ML of dissociated water molecules is metastable. The dissociation of water molecules at the LAO surface can reduce and even close the gap between the VBM of the LAO surface and the conduction band minimum (CBM) of the STO, leading to a metallic interface. Remarkably, for the ground state and metastable adsorption configurations, electron carrier densities at the interface show a large difference. Based on our findings we make an attempt to reveal the mechanism of the mysterious IMT found by Cen et al.

2. Computational details

We carried out first-principles electronic structure calculations within the framework of density functional theory as implemented in the Vienna ab initio simulation package (VASP) [27]. The generalized gradient approximation (GGA) [28] for the exchange–correlation functional and the projector augmented wave method [29, 30] with a kinetic cutoff energy of 400 eV for the plane wave basis set were used. Test calculations with higher cutoff energies confirm that the cutoff energy of 400 eV is sufficient for the description of the total energies and densities of states. The n-type LAO/STO interface was modeled as a (2 × 2) supercell consisting of four STO(001) layers, three LAO layers, and a vacuum region of about 14 Å. Various coverages of water molecules were located at the AlO2-terminated surface. Dipole correction was employed to correct the errors of the electrostatic potential, atomic force and total energy caused by periodic boundary condition [31]. The in-plane lattice constant of the slab was constrained at the calculated equilibrium value of STO bulk (a = 3.94 Å). A (4 × 4 × 1) k-point grid was used for calculations of atomic structure optimization and a (6 × 6 × 1) k-point grid for electronic structure calculations. All atomic coordinates were fully relaxed until the atomic forces were less than 0.02 eV Å−1, except for the atoms in the bottom two STO layers, which were fixed in their bulk positions. A first-principles molecular dynamics simulation at T = 300 K was performed to search for the atomic structure of 2 ML of water molecules adsorbed at the surface. The nudged elastic band method was used to calculate the reaction paths of water molecule dissociation at the surface.

3. Thermodynamic stability of water adsorption

Figure 1 displays geometries of various adsorption configurations at different coverages, in which water molecules are either molecular or dissociated. For the molecular adsorption, for instance c(1/4, 0), the O atom of the water molecule sits on the Al atom, forming an Al–O bond, and two H atoms approach to two closely neighboring O atoms at the AlO2 layer. For the dissociative adsorption, for instance c(1/4, 1/4), two distinct hydroxyl groups are produced, one of which originates from the water molecule and sits on the Al atom, the other (O1–H1) lies in the AlO2 layer. For the configurations of no more than 1 ML coverage, water molecules are bound to the surface by valence bonds or ionic bonds. Once the coverage exceeds 1 ML, as shown in c(2, 1/2), the extra
molecules are loosely adsorbed at the surface by hydrogen bonds.

Since the IMT observed in Cen et al’s experiments happened in a humid ambient atmosphere at room temperature, to directly address the experimental results we first investigated the thermodynamic stability of various adsorption configurations in an ambient atmosphere at room temperature by comparing their surface free energies. We calculated the surface free energies by employing the first-principles thermodynamics approach [24], in which the surface is assumed to be in equilibrium with a humid ambient atmosphere characterized by the relative chemical potential of water vapor. The most stable configuration at a given relative chemical potential minimizes the surface free energy approximately defined as

\[ \gamma = 1 \frac{E_{\text{ad}} - E_{\text{bare}}}{A} - n_{\text{H}_2\text{O}}[E_{\text{H}_2\text{O(gas)}} + \Delta \mu_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}})]. \]

Here, \( E_{\text{ad}} \) is the total energy of the interface with \( n_{\text{H}_2\text{O}} \) adsorbed water molecules per surface area \( A \), \( E_{\text{bare}} \) is the total energy of the bare surface, \( E_{\text{H}_2\text{O(gas)}} \) is the total energy of a gaseous water molecule, \( \Delta \mu_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}}) \) is the relative chemical potential of the water vapor at temperature \( T \) and partial pressure \( p_{\text{H}_2\text{O}} \). The vibrational free energy and configuration entropy contributions are neglected in the definition of surface free energy. \( E_{\text{ad}}, E_{\text{bare}}, \) and \( E_{\text{H}_2\text{O(gas)}} \) were obtained from our first-principles calculations. \( \Delta \mu_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}}) \) follows from the ideal-gas relation

\[ \Delta \mu_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}}) = \Delta \mu_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}}^{\text{bare}}) + k_B T \ln \left( \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^{\text{bare}}} \right). \]

At standard pressure \( p_{\text{H}_2\text{O}}^{\text{bare}} = 1 \text{ bar} \) the relative chemical potential can be derived using

\[ \Delta \mu_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}}^{\text{bare}}) = \{ H(T, p_{\text{H}_2\text{O}}^{\text{bare}}) - H(0 \text{ K}, p_{\text{H}_2\text{O}}^{\text{bare}}) \} - T [ S(T, p_{\text{H}_2\text{O}}^{\text{bare}}) - S(0 \text{ K}, p_{\text{H}_2\text{O}}^{\text{bare}}) ], \]

where the enthalpy and entropy differences are obtained from thermochemical tables [32]. The ambient atmosphere at room temperature sets an upper limit for \( \Delta \mu_{\text{H}_2\text{O}} = -0.57 \text{ eV per water molecule} \), which corresponds to the relative chemical potential of water molecules in a water-saturated atmosphere (100% relative humidity) at room temperature. The chemical potential at any other relative humidity can be obtained from the above ideal gas relation. Figure 2 displays the surface free energies of various adsorption configurations varying with the relative chemical potential or corresponding relative humidity at room temperature. In the range of relative humidity varying from 0.01% to 100%, which almost covers all possible relative humidities of the ambient atmosphere, the most stable configuration is \( c(1, 3/4) \). The configurations with a lower water coverage, such as \( c(1/4, 1/4) \), can only exist in an extremely dry environment. Noticeably, the configuration \( c(2, 1/2) \) with 2 ML of water has a higher free energy than \( c(1, 3/4) \) and even than \( c(1, 1/2) \). This implies that once the coverage reaches 1 ML the surface will no longer adsorb water molecules from the atmosphere, instead, water molecules readily remain in the atmosphere.

4. Adsorption of 1/4 ML of water molecules: dissociation process and electronic properties

For simplicity and clarity we first explored the dissociation process of 1/4 ML of water molecules adsorbed at the LAO surface and its effect on the electronic properties of the interface system. Figure 3(a) displays the process without an energetic barrier for 1/4 ML of water molecules at the LAO surface, in which the binding energy is defined as \( E_{\text{b}} = E_{\text{ad}} - E_{\text{bare}} - n_{\text{H}_2\text{O}} \cdot E_{\text{H}_2\text{O(gas)}} \). The intermediate state involves a four-member ring Al–Ow–H1–O1. Generally, water molecule dissociation at metal oxide surfaces is associated with the breaking of the metal–oxygen bond at the surface [17, 21, 22, 24, 33], implying that the dissociation occurs more easily.
Figure 2. Surface free energies of various adsorption configurations at the LAO surface as functions of the relative chemical potential of water vapor, \( \Delta \mu_{H_2O} \). The top axis shows the relative humidity of the ambient atmosphere at 300 K corresponding to the relative chemical potential on the bottom axis. The free energy of the bare surface is taken to be zero.

Figure 3. (a) Dissociation process of 1/4 ML of water molecules adsorbed at the AlO\(_2\)-terminated surface of the LAO/STO interface. The reaction coordinate is the distance \( d_{O1-H1} \) between the hydrogen atom H1 and the oxygen atom O1. Insets are perspective views for molecular, intermediate and dissociative configurations. (b), (c) Projected densities of states (PDOSs) for the O1 atom in (b) the molecular (mol) and (c) dissociative (dis) adsorption configurations of 1/4 ML coverage, respectively. The vertical lines denote the Fermi level. The VBM of the STO bottom layer is taken to be zero (see figure 4). The \( x \) and \( y \) axes are approximately along the direction of Al–Os–Al chain and that of Al–O1–Al chain shown in the insets in (a).

at a surface with loose metal–oxygen bonds. Indeed, the Al–O bond at the LAO surface is far weaker than that of \( \alpha\)-Al\(_2\)O\(_3\). This fact is reflected by the bond lengths in these two materials, 1.95 Å (in-plane) for the former and 1.70 Å for the latter [22]. This implies that the energy cost to stretch the Al–O1 bond in the four-member ring is relatively low and can be compensated by the formation of a hydroxyl O1–H1 bond. To reveal the driving force of water molecule dissociation at the LAO surface we checked on the change of electronic states of the O1 atom in both molecular and dissociative adsorptions. In molecular adsorption (figure 3(b)) the \( p_z \) orbital of O1 is a non-bonding state lying near the top of the valence band. While in dissociative adsorption (figure 3(c)) the bonding state of the hydroxyl O1–H1, mixing part states of \( p_z \) and \( p_y \) orbitals, lies at the bottom of valence band. The lower surface energy of dissociative adsorption just arises from the drop of the band energies of these O p states. Therefore, we see in figure 2 that for the configuration of 1 ML coverage the surface free energy decreases with increasing coverage of dissociated molecules up to 3/4 ML. The energy rise of 1 ML of dissociated water molecules is due to a large structural distortion at the surface.

Figure 4(a) shows layer-resolved projected densities of states (LPDOSs) of molecular and dissociative adsorptions of...
1/4 ML coverage. We note that water molecule dissociation gives rise to a remarkable change of electronic states of the surface layer; compared to molecular adsorption, the VBM of the LAO surface layer shifts up by about 0.2 eV in dissociative adsorption. The PDOSs in figures 4(b) and (c) show that this up-shift is mainly due to the up-shift of the p$_z$ orbital of the O atoms, like the Os atom near the hydroxyl Ow–H. We ascribe this up-shift to an extra repulsive Coulomb potential generated by the negatively charged hydroxyl Ow–H. As shown in figures 4(d) and (e), compared to molecular adsorption, in dissociative adsorption the potential energy over the Os atom rises significantly, implying that the p$_z$ orbital of the Os atom lies at a higher position. Moreover, our calculations show that as more water molecules dissociate the VBM of the LAO surface layer shifts up more. A coverage of dissociated water molecules as high as no less than 1/2 ML can even lift the VBM of the LAO surface layer by about 0.6 eV, consequently closing the gap between the VBM of the LAO surface layer and the STO CBM and thus leading to a metallic interface.

5. Adsorption of 1 ML of water molecules: dissociation process and electronic properties

Dissociation processes of 1/2, 3/4 and 1 ML of water molecules adsorbed on the LAO surface were also investigated. We found that for all of them there is an upper limit of coverage of water molecules that dissociate without a barrier, 1/2 ML. Here we are most interested in the case of 1 ML coverage because c(1,3/4), a configuration of 1 ML coverage, is the thermodynamic ground state in an ambient atmosphere at room temperature and, as shown below, the change of electronic properties of the LAO/STO interface during the dissociation process of 1 ML of water molecules can be compared with the thermal results. Figure 5 shows the energy profile of a reaction path for the dissociation of 1 ML of water molecules, in which four water molecules dissociate one by one. We note that the barrierless dissociation of the preceding two water molecules induces a large distortion at the surface. This distortion greatly increases the distance between the hydrogen atom H3 of the third water molecule and the oxygen atom O3 at the LAO surface, finally giving rise to an energy barrier of 0.1 eV in the dissociation path of the third water molecule. Furthermore, the dissociation of the fourth water molecule encounters an even higher barrier of 0.41 eV and the association of this dissociated molecule encounters a barrier of 0.17 eV.

To clearly see the effect of the dissociation of 1 ML of water molecules on the electronic properties of the LAO/STO interface we plot LPDOSs in figure 6(a) for 1 ML coverage.
PDSs of water molecules and the LAO surface layer present apparent differences in the molecular and dissociative adsorptions. In the fully molecular adsorption three molecular orbitals of water molecule corresponding to three peaks ranging from $-7$ to $-2$ eV are very well preserved. This molecular adsorption barely affects the electronic states of the LAO surface, the band gap between the VBM of the LAO surface and the CBM of the STO is 0.54 eV, approximately the same as the value of the interface with a bare surface, 0.56 eV. In contrast, water molecule dissociation significantly modifies the electronic states of the LAO surface and the interface. Accompanying the dissociation, the VBM of the LAO surface layer shifts up considerably and a surface state originating from the hydroxyls on Al atoms appears at the VBM. Strikingly, the dissociation of no less than 0.5 ML of water molecules closes the band gap, resulting in a metallic interface. Figure 6(b) shows the details of the electronic states of water molecules and the LAO surface layer near the Fermi level. Since the VBM of the LAO surface layer and the water molecules exceeds the STO CBM, a part of the charge transfers from the surface into the STO conduction band. The carrier density is equal to the density of the empty states in the valence band shown in figure 6(b). As shown in figure 6(c), the carrier density increases with increasing coverage of dissociated water molecules. The carrier density is $1.3 \times 10^{13}$ cm$^{-2}$ for $c(1, 3/4)$, and reaches to its highest value, $1.9 \times 10^{13}$ cm$^{-2}$, for $c(1, 1)$.

6. Discussions

The above calculated results are schematically illustrated in figure 7. The electronic properties at the LAO/STO interface are almost unaffected by molecular adsorption of water molecules at the LAO surface. Dissociative adsorption shifts up the p states of the O atoms (like Os) neighboring the hydroxyl Ow–H on the Al atom, and induces a state originating from the hydroxyl Ow–H at the VBM of the LAO surface. Once the coverage of dissociated water molecules reaches 1/2 ML, the VBM of the surface exceeds the STO CBM, resulting in a charge transfer from the surface to the conduction band of the STO. In ambient atmosphere at room temperature $c(1, 3/4)$ is the ground state and has a lower carrier density, while $c(1, 1)$ is metastable and has a higher carrier density. This implies that a structural transition between these two stable adsorption configurations can induce a conductance change at the LAO/STO interface. This picture provides us a way to interpret the mechanism of the IMT observed by Cen et al. But, before elucidating it we should first clarify so-called insulator state in their experiment. In fact, before the AFM tip scans the LAO surface the interface is already metallic and has a carrier density change at the LAO/STO interface induced by different water adsorptions can only happen in the case of three LAO layers, being in good agreement with Cen et al’s experimental result. For the interface between two LAO layers the calculated gap between the VBM of the LAO surface layer and the STO CBM is 1.1 eV, which is too large to be closed by water molecule adsorption because the VBM up-shift due to water adsorption is only about 0.6 eV. In the case of four LAO layers, the interface is already metallic and has a carrier density of $2 \times 10^{13}$ cm$^{-2}$, as reported by Thiel et al [5], which may smooth over the carrier density change due to the different adsorption configurations.

Considering this point and associating the conductance change observed in Cen et al’s experiment with the difference of carrier densities of two stable adsorption configurations, $c(1, 3/4)$ and $c(1, 1)$, we propose a mechanism as the following. Before the AFM tip scans the LAO surface the configuration of water molecules lies at the thermodynamic ground state $c(1, 3/4)$, and the interface shows a relatively low conductance. After the AFM tip with positive voltages scans the LAO surface all water molecules in the scanned area dissociate, i.e., the configuration of water molecules in the scanned area becomes $c(1, 1)$, thus the interface shows a higher conductance. As for how the AFM tip dissociates water molecules, a recent study on water molecule dissociation at a MgO surface by means of STM tip scanning has provided a possible answer [33]. It was demonstrated that a tunneling current passing through the adsorbed water molecule can induce a lateral vibration model of the water molecule, consequently facilitating the dissociation. Therefore, it is highly possible that in Cen et al’s experiment water molecules in the area scanned by the AFM tip were fully dissociated due to a tunneling current passing through them.

Moreover, according to our calculations the carrier density change at the LAO/STO interface induced by different water adsorptions can only happen in the case of three LAO layers, being in good agreement with Cen et al’s experimental result. For the interface with two LAO layers the calculated gap between the VBM of the LAO surface layer and the STO CBM is 1.1 eV, which is too large to be closed by water molecule adsorption because the VBM up-shift due to water adsorption is only about 0.6 eV. In the case of four LAO layers, the interface is already metallic and has a carrier density of $2 \times 10^{13}$ cm$^{-2}$, as reported by Thiel et al [5], which may smooth over the carrier density change due to the different adsorption configurations.

64x141, and after the AFM tip scans the surface the conductance rises to about 7.6 nS. The conductance change at the LAO/STO interface is about ten per cent. In comparison with the approximately five orders of magnitude resistance difference between the insulating and metallic interfaces reported by Thiel et al [5], the interface with 6.9 nS conductance should rather be regarded as metallic.

Figure 7. Schematic atomic structures and band diagrams of the LAO/STO interface with water adsorption on the surface. (a), (b) Molecular adsorption, and (c), (d) dissociative adsorption. Shaded areas are the valence bands of the STO and LAO. Red and pink filled curves present O p states of the LAO surface layer, blue filled curves represent the states of water molecules.
Noticeably, besides the aforementioned mechanism of conductance change at the LAO/STO interface, our results also imply another scheme to realize a sharper switch between insulating and metal states at the LAO/STO interface with three LAO layers by adsorbing and desorbing water molecules at the LAO surface. In this scheme the insulating state corresponds to the case of a bare surface and the metallic state corresponds to an adsorption configuration of 1 ML of water molecules adsorbed at the surface. The insulator–metal transition can be realized by exposing the bare surface to a water vapor and the reverse transition can be realized by desorbing the water molecules from the surface.

7. Summary

In summary, we have studied the electronic and structural characteristics of water molecule adsorption on the LAO surface of the n-type LAO/STO interface by using first-principles electronic structure calculations. We found that in an ambient atmosphere at room temperature the adsorption configuration of 1 ML of water molecules including 3/4 ML of dissociated molecules is most stable and the configuration of 1 ML of dissociated water molecules is metastable. For the LAO/STO interface with three LAO layers, dissociation of no less than 0.5 ML of adsorbed water molecules results in a metallic interface, and the carrier density increases with increasing coverage of dissociated water molecules. A structural transition between the ground state and metastable water adsorption configurations can induce a carrier density change at the LAO/STO interface. Our findings provide new insights into creating and modulating electron carriers at the LAO/STO interface, which will hopefully prompt the insights into creating and modulating electron carriers at the LAO/STO interface.

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