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ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.5b01698 • Publication Date (Web): 12 May 2015

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Evolution of the SrTiO₃/MoO₃ interface electronic structure: An *in situ* photoelectron spectroscopy study

Yuanmin Du[†], Hai Yang Peng[§], Hongying Mao^{‡,¶}, Ke Xin Jin[⊥], Hong Wang[†], Feng Li[†], Xing Yu Gao^{&,§}, Wei Chen^{‡,&,*}, Tom Wu^{†,*}

[†]*Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia*

[§]*Advanced LSI Technology Laboratory, Corporate Research and Development Center, Toshiba Corporation, Kawasaki 212-8582, Japan*

[‡]*Department of Chemistry, National University of Singapore, 2 Science Drive 3, 117542 Singapore*

[¶]*Department of Physics, Hangzhou Normal University, Hangzhou 310036, P. R. China*

[⊥]*Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, P. R. China*

[&]*Department of Physics, National University of Singapore, 2 Science Drive 3, 117542 Singapore*

[§]*Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, P. R. China*

ABSTRACT:

Modifying the surface energetics, particularly the work function, of advanced materials is of critical importance for a wide range of surface- and interface-based devices. In this work, using *in situ* photoelectron spectroscopy, we investigated the evolution of electronic structure at the SrTiO₃ surface during the growth of ultrathin MoO₃ layers. Thanks to the large work function difference between SrTiO₃ and MoO₃, the energy band alignment on the SrTiO₃ surface is significantly modified. The charge transfer and dipole formation at the SrTiO₃/MoO₃ interface leads to a large modulation of work function and an apparent doping in SrTiO₃. The measured evolution of electronic structure and upward band bending suggest that the growth of ultrathin MoO₃ layers is a powerful tool to modulate the surface energetics of SrTiO₃, and this surface-engineering approach could be generalized to other functional oxides.

KEYWORDS: SrTiO₃; MoO₃; photoelectron spectroscopy; charge transfer; work function

INTRODUCTION

Being a prototypical perovskite-structured transition-metal oxide, SrTiO₃ (STO) has attracted a great deal of interest in the field of oxide electronics.¹⁻¹¹ Although stoichiometric STO is an excellent band insulator with a wide band gap of 3.2-3.3 eV,¹² metallic conduction can be readily achieved by cation substitution or oxygen reduction (e.g. thermally or electrically).^{13,14} Thanks to the highly tunable transport property of STO and low activation energies of ionic migrations, a wide range of high-impact electronic devices have been realized. Particularly, resistive switching devices have been demonstrated as a promising nonvolatile memory technology where the resistance states are controlled by an external electrical field.⁶⁻¹⁰ For example, Choi *et al.* studied the resistive switching effect in a Pt/STO/Si heterostructure, and attributed it to the change of electrical property at the Pt/STO interface as a result of interfacial charge transfer.⁸ Furthermore, such interface-modulated resistive switching has been extensively reported for other transition-metal oxides.¹⁵⁻²² In these breakthroughs, electronic structures and physical properties of STO-based interfaces are important in the functionalization of oxide electronics. Hence, a deep understanding of charge transfer and interfacial band alignment is the key to further improve the performance of functional devices based on STO and other oxides. There are generally evolutions of interfacial electronic structures, particularly charge transfer and dipole formation, when two conducting or semiconducting materials with different work functions get in touch.²³ Such a surface-charge-transfer doping strategy was recently applied to compound semiconductors with a focus on organic optoelectronic devices,²⁴ but it has not been explored for the prototypical oxide STO.

Among various metal oxides, molybdenum trioxide (MoO₃) is an environmentally friendly material which has been extensively studied in the fields such as electrochromism, batteries,

gas sensors, switching memories and organic optoelectronics.²⁵⁻³⁸ As a wide band gap material, the band gap of MoO₃ has been reported to be 2.9-3.0 eV.^{25, 39} Oxygen deficiency in stoichiometric MoO₃ leads to occupied defect states close to the conduction band minimum, making it an n-type semiconductor. With the Fermi level lies close to the conduction band minimum, a strong n-type semiconductor property has also been reported for MoO₃.³⁹ Thanks to its very high work function (6.8 eV), MoO₃ was widely used to modify the metal/organic interfaces, and a mechanism of hole injection *via* electron extraction has been proposed.²⁹⁻³⁹ Furthermore, in contrast to some chemically active metals, MoO₃ is not expected to react with oxide semiconductors, thus it is an ideal choice for investigating interfacial electronic structures.

In this report, we demonstrate effective charge transfer at the STO/MoO₃ interface as a result of the large work function difference between STO and MoO₃, and the interfacial band alignment was probed using *in situ* ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS). To the best of our knowledge, *in situ* photoelectron spectroscopy techniques have not been applied to the STO/MoO₃ interface although both materials are among the most intensively pursued oxide semiconductors. The observed evolution of charge transfer and dipole formation provides valuable insights on the properties of the STO/MoO₃ interface as a “model” system, which will facilitate the applications of STO and other oxides in advanced electronic devices.

EXPERIMENTAL SECTION

The preparation of the samples and photoelectron spectroscopy (PES) measurements were carried out *in situ* in a multi-chamber ultrahigh vacuum (UHV) system.⁴⁰ (001)-oriented STO single crystals (one-side polished, $10 \times 10 \times 0.5 \text{ mm}^3$) with TiO_2 termination were annealed at 650°C in high vacuum ($< 10^{-7}$ mbar) for 10 minutes. Then MoO_3 thin films were thermally evaporated onto the STO substrate from a Knudsen cell in the growth chamber with a base pressure better than 3×10^{-9} mbar. The deposition temperature was 400°C , monitored by a thermal couple at the bottom of the Knudsen cell. The deposition rate of MoO_3 (0.2 nm/min) was monitored by a quartz crystal microbalance (QCM). XPS measurements were performed with Al K α source ($h\nu = 1486.6 \text{ eV}$). UPS measurements were performed with He I ($h\nu = 21.2 \text{ eV}$) as the excitation source. During the UPS measurements, a sputtered clean gold foil was in contact with the sample. Binding energies of all PES spectra were referenced to the Fermi level of the gold foil. The work function of the analyzer is 4.3 eV in the UPS/XPS system. Vacuum level shifts (changes of work function) were measured from the linear extrapolation of the low kinetic energy part of the UPS spectra with a -5 V sample bias.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of Sr 3*d*, Ti 2*p* and O 1*s* peaks as a function of increasing MoO_3 thickness on STO. The Sr 3*d* and the Ti 2*p* spectra of the clean STO surface are dominated by the Sr 3*d* peak centered at $133.4 \pm 0.05 \text{ eV}$ and the Ti 2*p* peak centered at $459.0 \pm 0.05 \text{ eV}$, respectively. These peak positions are consistent with the report in literature.⁴¹ Upon the initial deposition of MoO_3 with a nominal thickness of 0.2 nm, a shift of about 0.6 eV for both peaks toward lower binding energies was observed, indicating an

upward band bending or a charge (hole) transfer from MoO_3 to STO. Further increases of MoO_3 thickness produced less notable effects on the peak shift. Because the work function of MoO_3 is much higher than that of STO, the charge transfer at the STO/ MoO_3 interface is expected to result in the accumulation of holes in the STO layer. This energy shift as a result of MoO_3 deposition is much larger than the value of 0.2 eV reported previously for the STO surface upon the oxygen exposure,^{42,43} indicating a much stronger electron transfer at the STO/ MoO_3 interface (hole doping in STO).

Figure 1. XPS core-level spectra during the deposition of MoO_3 on SrTiO_3 : (a) Sr 3d, (b) Ti 2p, (c) O 1s. (d), (e) and (f) O 1s spectra of a bare SrTiO_3 substrate, and the STO/ MoO_3

interfaces with nominal MoO₃ thicknesses of 0.2 nm and 5 nm. Solid lines represent the Gaussian/Lorentzian mixed functions used for fitting to the experimental data (black dots).

The evolution of the O 1s XPS spectra gave valuable insights on the electronic structures of the STO/MoO₃ interface. Figure 1(c) shows the evolution of the O 1s XPS spectra as a function of MoO₃ thickness. The peak positions of the spectra are marked in the Figure 1(c) as A-F. A notable shift to lower binding energies was observed at the initial deposition. The peak shift was inverted at the subsequent deposition and the O 1s peak position demonstrated an upward trend as the MoO₃ deposition thickness increased from 0.4 nm to 5 nm. A transition of symmetric → asymmetric → symmetric characteristic of the O 1s peak was observed. To shed light on this behavior, we applied Gaussian/Lorentzian fitting to the O 1s peaks. As shown in Figure 1(d), the O 1s spectrum of the bare STO substrate can be fitted with three sub-peaks. The component (O_s) located at the binding energy of 530.1 eV is originated from the lattice oxygen in STO, and this component shifts by 0.6 eV to a lower binding energy (529.5 eV) upon the 0.2 nm MoO₃ deposition (Figure 1(e)). The peak at 531.8 eV (O_c) is assigned to oxygen ions in oxygen deficient regions, i.e., oxygen vacancies.^{44, 45} Similar to the O_s component, this peak shifts to a lower position at 531.2 eV after the MoO₃ deposition. The existence of oxygen vacancies is consistent with the high temperature annealing process (650 °C in high vacuum for 10 minutes), and the oxygen vacancies donate electrons and strongly improve the STO conductivity. First-principles calculations by Shen *et al.*⁴⁶ showed that metallic states can be achieved by introduction of oxygen vacancies. Using Ar⁺ ions irradiation, Sánchez-Santolino *et al.* also reported metallic states in STO.⁴⁷ The

MoO₃ deposition also leads to the appearance of a peak at 530.0 eV (O_b), as shown in Figure 1(e), which is related to the lattice oxygen in MoO₃. The co-existence of O_s, O_b and O_c leads to the asymmetric shape of the O 1s peaks. In contrast to Figure 1(d), the O_s peak from the STO substrate significantly decreases after the MoO₃ deposition, while the MoO₃-related O_b peak increases. When the MoO₃ thickness finally increases to 5 nm, the O 1s spectrum is dominated by the O_b component, as shown in Figure 1(f). Overall, the XPS spectra indicate that multiple oxygen states are formed at the STO/MoO₃ interface, and these states evolve with the MoO₃ thickness. Furthermore, the transition between the asymmetric and symmetric characteristics of the O 1s peaks with increasing MoO₃ thickness, particularly the significant suppression of the O_c peak, indicates that substantial oxidation takes place during the MoO₃ deposition.

The transition of Mo oxidation states at the interface was further supported by the Mo 3d core level spectra shown in Figure 2(a). With the MoO₃ thicknesses of 0.4 nm and 1.5 nm as examples, the spectra are fitted with two oxidation states, i.e., Mo⁶⁺ and Mo⁵⁺ states, each comprising of two peaks (3d_{5/2} and 3d_{3/2}) due to the spin-orbit splitting. In the fitted spectra shown in Figures 2(b) and 2(c), the energy separation between 3d_{5/2} and 3d_{3/2} was fixed at 3.1 eV. The 3d_{5/2} binding energies of Mo⁶⁺ and Mo⁵⁺ states are located at 232.2±0.05 eV and 231.3±0.05 eV, respectively, consistent with the previous reports.^{48, 49} With increasing MoO₃ thickness, the regular Mo⁶⁺ state becomes dominant, and the relative content of Mo⁵⁺ state decreases, indicating that the lower oxidation state mostly exists at the interface due to the electron transfer from STO to MoO₃ in the interface region. When the MoO₃ thickness increases to 5.0 nm, the Mo 3d core-level spectrum is dominated by the Mo⁶⁺ feature.

Figure 2. (a) Evolution of the Mo 3d core level as a function of the MoO₃ thickness. (b) and (c) Fitting of the Mo 3d spectra at nominal thicknesses of 0.4 nm and 1.5 nm. The green and red lines represent Mo⁶⁺ and Mo⁵⁺ components, respectively. Solid lines and square symbols represent the fitting results and the experimental data, respectively.

Understanding the interfacial energy level alignment is important for device optimization. The changes of secondary electron cutoff with increasing MoO₃ thickness are plotted in Figure 3(a). The deposition of MoO₃ on STO shifts the energy cutoff towards lower kinetic energies, i.e., increasing the “effective” work function of the STO substrate. In the measurements, an energy difference of 0.7 eV exists between the work function and the kinetic energy. Figure 3(a) shows that the initial STO substrate has a work function of 3.6 eV, which is close to the value reported in literature.⁵⁰ A significant change of work function (1.6 eV) was observed at a nominal MoO₃ deposition thickness of 0.2 nm. When the MoO₃ deposition proceeds further to the thickness of 5 nm, the work function increases and finally saturates at 6.8 eV, that is, a large change of 3.2 eV. This final work function is the same as

MoO₃,³⁹ indicating that bulk-like MoO₃ is formed on STO. The large work function difference between MoO₃ and STO results in a significant electron transfer from STO to MoO₃, and hence large interface dipoles form at the STO/MoO₃ interface.

Figure 3. (a) UPS spectra in the low-kinetic energy region (secondary electron cutoff) and (b) valence band spectra as a function of the MoO₃ thickness. (c) Close-up of the near-Fermi-level region of the valence band. (d) Evolutions of the work function and the core-level bending as a function of the nominal MoO₃ thickness.

Figure 3(b) shows the evolution of the valence band edge of STO thin films with the increasing coverage of MoO₃. The valence band (VB) edge of STO is located at 3.4 eV below the Fermi level. Since the SrTiO₃ band gap is ~ 3.2 eV, the Fermi level is very close to the conduction band minimum, which is consistent with the metallic nature of the annealed STO substrate. The high-temperature annealing process produces lots of electron-donating oxygen vacancies, leading to the metallic state of STO. The dominant components below the edge, located between 3.0 and 10.0 eV, mainly come from the O *2p* derived states.^{49, 51} With

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4 increasing MoO₃ thickness, the VB edge moves closer to the Fermi level. From the VB edge
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6 of MoO₃ at 2.7 eV, an ionization energy of 9.5 eV can be derived, consistent with previous
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8 reports.⁵² A close-up view of the region near the Fermi level of the VB spectra (0.2 nm to 1.5
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10 nm) is shown in Figure 3(c). With the MoO₃ deposition, broad gap states can be clearly
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12 observed in the band gap, located between the VB edge and the Fermi level. These gap states
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14 could come from surface oxidation, consistent with the previous reports.⁵³⁻⁵⁵
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19 In Figure 3(d), the evolutions of work function and core-level banding energy are plotted
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21 as a function of the MoO₃ coverage. After a significant change at the nominal MoO₃
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23 thickness of 0.2 nm, the work function gradually increases until a thick MoO₃ layer is formed.
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25 In contrast, after a sudden change of 0.6 eV at the initial 0.2 nm, the band bending of STO
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27 remains constant with further MoO₃ deposition. Although 0.2 nm is the minimum thickness
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29 in our experiments, we believe that a gradual shift should occur for MoO₃ thicknesses smaller
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31 than 0.2 nm, and further measurements will be carried out in future. Here, we propose that
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33 band gap states play a key role in the evolution of electronics structure of STO surface. As a
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35 result of interfacial charge transfer, the oxygen vacancies on the STO side become positively
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37 charged, while electrons are trapped at the igap states on the MoO₃ side, forming a negative
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39 charge zone. Such dipoles inhibit any further charge injection when the equilibrium is
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41 established, significantly affecting the electronic structure of the STO/MoO₃ interface. As
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43 shown in Figure 3(d), the significant increase of the work function contains contributions
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45 from the bending of the STO band near the interface.⁵⁶ However, throughout the MoO₃
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47 growth, the increase of the work function is substantially larger than the VB bending,
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49 indicating that the work function shift mainly comes from the interface dipoles.
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Figure 4. (a) Schematic illustration of charge transfer at the SrTiO₃/MoO₃ interface. (b) Energy level alignment scheme of the SrTiO₃/MoO₃ interface. VL – vacuum level, CB – conduction band, VB – valence band, and E_F – Fermi level.

The large difference of work function between STO and MoO₃ leads to significant charge transfer at the interface (Figure 4(a)). As a result, an electron-depleted layer is formed on the STO side, while an electron-accumulated layer is formed on the MoO₃ side. The work function of the STO substrate is significantly modulated by the ultrathin MoO₃ layers. Based on the results of UPS and XPS measurements, an energy level diagram of the STO/MoO₃ interface is depicted in Figure 4(b). In the schematic energy diagram, band gap values of 3.2 eV and 2.9 eV are used for STO and MoO₃, respectively. The Fermi level is aligned across the interface in the thermodynamic equilibrium state. Initially, the STO substrate after annealing exhibits the metallic property. Upon the deposition of MoO₃, electrons transfer from STO to MoO₃, and equivalently holes are doped into the STO surface, leading to an upward band bending. As a consequence, the Fermi level at the STO surface is located between CB and VB, indicating significant modification of the interfacial electrical property.

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4 Concurrently, the electron transfer and doping in the MoO₃ side leads to a downward band
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6 bending.
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9 We should note that the upward band bending at the STO/MoO₃ interface observed in this
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11 work is opposite to the downward band bending extensively reported for two-dimensional
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13 electron gas formed at the STO surfaces/interfaces.³⁻⁵ Electron-donating oxygen vacancies
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15 are extensively reported to abundantly exist in STO-related systems. On the other hand, in
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17 our experiments, the evolution of the O 1s peaks as a function of increasing MoO₃ thickness,
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19 as shown in Figure 1, indicates the occurrence of substantial oxidation and hole doping.
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21 Similar charge transfer and band bending effect could also be induced by an electric field.⁵⁷
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23 Thus, our report is complementary to these reports in literature, and this surface transfer
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25 doping strategy clearly warrants further investigations.
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32 As shown in Figure 4, with increasing MoO₃ thickness, large interface dipoles emerge.
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34 The underlying mechanism behind the observed maximum band bending of 0.6 eV could be
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36 due to the formation of high-density gap states at the interface, which inhibits any further
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38 hole injection into the STO surface layer. These interface states may be similar to the metal-
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40 induced gap states (MIGS) proposed for the conventional metal-semiconductor junction,⁵⁸
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42 but more work is required to understand their physical origin and the role of interface states
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44 in the process of charge transfer. Nevertheless, the large change of work function via
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46 modulating the MoO₃ overlayer thickness provides an effective approach to control the
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48 interface barrier and the surface properties of STO-based electronic devices.
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56 57 CONCLUSIONS 58 59 60

In summary, the electronic structure of the STO/MoO₃ interface has been investigated for the first time using *in situ* photoemission spectroscopy. The deposition of high work function MoO₃ thin film results in a hole-accumulation layer at the STO surface. A maximum band bending of 0.6 eV was observed, and the work function of STO substantially increased after the deposition of MoO₃. These results indicate the potential use of MoO₃ as an effective material to induce charge transfer and to tune the oxide work functions. This surface/interface engineering technique may be generalized to other oxides and heterostructures, enhancing the performance of oxide electronic devices.

AUTHOR INFORMATION

Corresponding Author

*Email: phycw@nus.edu.sg.

*Email: tao.wu@kaust.edu.sa.

ACKNOWLEDGEMENTS

Authors acknowledge the financial support from Singapore MOE Grant R143-000-559-112.

Research reported in this publication was also supported by the King Abdullah University of Science and Technology (KAUST).

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