Understanding the Exotic Properties of Perovskite Oxide Heterostructures using Density Functional Theory

Zhou Jun

Department of Physics, National University of Singapore, Singapore

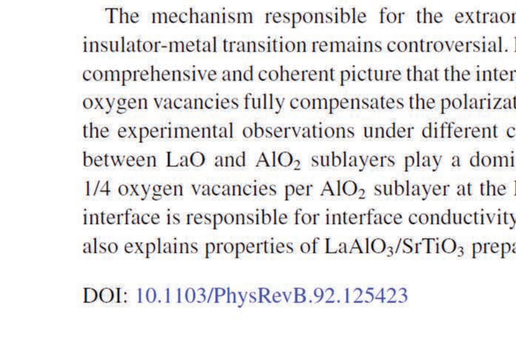
ZHOU JUN

Achievements

Mr Zhou carried out first-principles calculations to address some important and challenging issues related to two-dimensional (2D) electron gas at the interface of oxides. The interface of dissimilar oxide materials has been a hot research topic in recent years because of the rich varieties of exotic phenomena not found in its constituent materials. Being a talented researcher, with a good understanding in fundamental physics, Mr Zhou came up with many of his own ideas which turned out to be crucial in understanding the computational and experimental results.

Awards

- ✓ Best Poster Award of the conference during the 9th International Conference on Computational Physics (ICCP9) held in Singapore in January 2015
- ✓ Winner of the NUS FoS Best Graduate Researcher Award from Physics (2016)



Publication Highlights

Introduction

- The interface of dissimilar oxide materials hosts rich varieties of exotic phenomena not found in its constituent materials. For example, both bulk $LaAlO_3$ (LAO) and bulk $SrTiO_3$ (STO) are wide-band-gap nonmagnetic insulators. Remarkably, when LAO was deposited on STO (001), the interface was found to exhibit unusual phenomena such as a conducting two dimensional electron gas, superconducting and magnetic properties, and two-dimensional coexistence of both superconducting and magnetic properties.
- In particular, the mechanism responsible for the extraordinary interface conductivity of LAO/STO in both (001) and (110) orientations, as well as the remarkable interface magnetic orderings remains hotly debated. In this thesis, we established a comprehensive understanding of the electronic and magnetic reconstructions at LAO/STO interfaces.
- With these extraordinary properties, perovskite oxide interfaces are very promising for all-oxide electronics. In this thesis, we designed an oxide system, *i.e.* metal capped $BaTiO_3/SrTiO_3$ (BTO/STO) with tunable interface conductivity, promising for non-volatile memory applications.

Methodology

- First-principles method based density functional theory (VASP).
- Projector-augmented wave (PAW) potentials.
- Generalized gradient approximation (GGA) for electronic properties.
- On site Coulomb interaction (+U) for magnetic properties
- Local density approximation (LDA) for BTO/STO calculations.

Insulator-metal transition of LAO/STO (001) & (110)

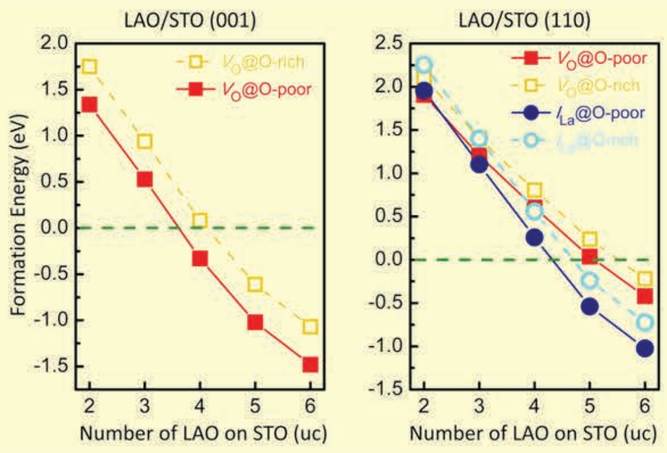


Fig. 1 Formation energies (E_f) of possible polar-induced defects in LAO/STO (001) & (110)

Considering the different structure of LAO/STO in (001) (planar) and (110) (buckled) orientations, we propose possible polar-induced defects, *i.e.* surface oxygen vacancies (V_O) for (001) and surface V_O as well as surface La interstitial defects (I_{La}) for (110) heterostructures.

The LAO-thickness dependent formation energy of surface V_O becomes negative after 4 uc for (001) in both O-rich and O-poor conditions. While in (110), surface I_{La} are more promising than V_O (lower formation energy).

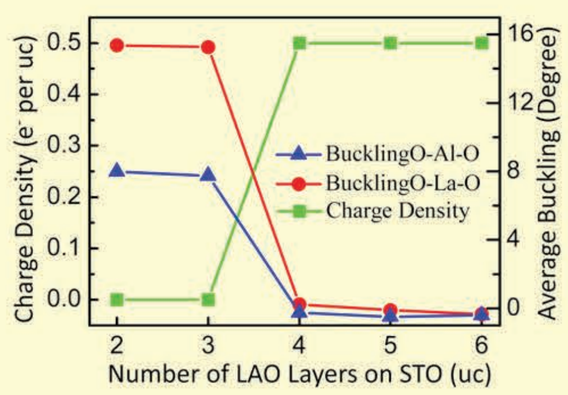


Fig. 2 The different mechanisms to compensate the polar divergence of LAO/STO with thin (< 4uc) and thick (≥ 4 uc) LAO thicknesses.

Depending on the E_f calculations, we propose buckling effects between cations and oxygen atoms, and surface defects [V_O for (001), I_{La} for (110)], which fully compensate the polar divergence, to explain the *step-like* insulator-metal transition of LAO/STO with LAO thickness.

Room-temperature magnetism in LAO/STO (001)

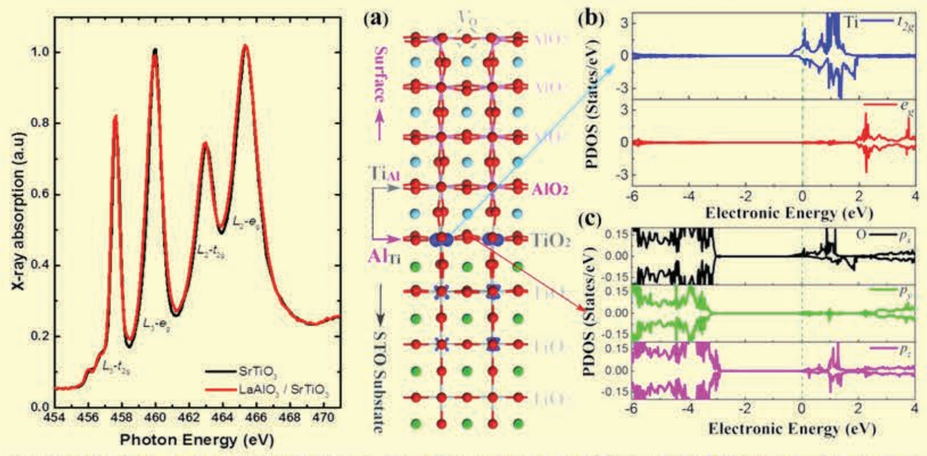


Fig. 3 XAS at Ti $L_{3,2}$ edges of bulk STO and room-temperature magnetic LAO/STO.

Fig. 4 The structure and PDOS of LAO/STO with surface V_O and interface (Ti_{Al}+Al_{Ti}) anti-site defects.

We find room-temperature magnetism in LAO/STO samples grown at high oxygen partial pressure. By comparing the XAS with bulk STO, we attribute this magnetism to the interplay of surface V_O and (Ti_{Al}+Al_{Ti}) interface defects.

Metal capped BTO/STO with tunable interface conductivity

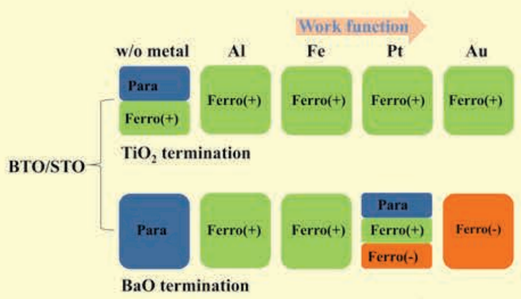


Fig. 5 Possible polarization states of BTO in BTO/STO with different metal capping layers.

We find the different metal capping layers have dramatic influence on the polarization states of BTO. In particular, with Pt capping layers, the BTO/STO interface can be tuned from insulating, hole- or electron-conducting states, promising for future electronic applications.

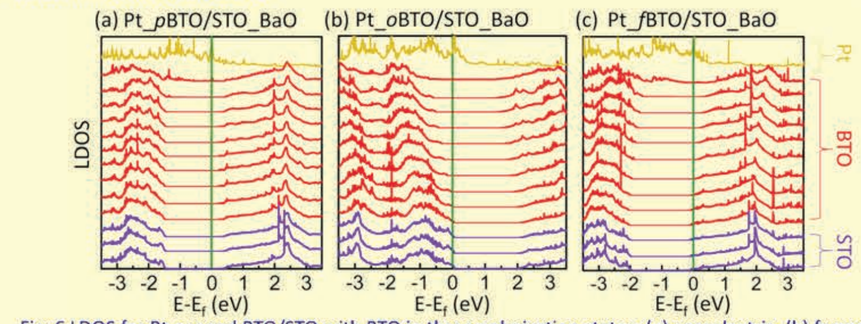


Fig. 6 LDOS for Pt-capped BTO/STO with BTO in three polarization states: (a) paraelectric, (b) ferroelectric with polarization pointing to Pt/BTO interface, (c) ferroelectric with opposite direction with (b).

Conclusions

In this thesis, using density functional theory calculations, we shed light on the mechanisms responsible for the insulator-metal transition of LAO/STO in both (001) and (110) orientations, as well as for the room-temperature strong magnetism in LAO/STO (001). Besides, we predict a perovskite oxide heterostructure with tunable interface conductivity, promising for future electronic applications.

Supervisors: Prof. Yuan Ping Feng, Prof. Andrivo Rusydi.

References: PRB **92**, 125423 (2015); PRB **93**, 155167 (2016)

Acknowledge NUS Computer Centre and Centre for Advanced 2D Materials for computational support.

PHYSICAL REVIEW B **92**, 125423 (2015)

Interplay of electronic reconstructions, surface oxygen vacancies, and lattice distortions in insulator-metal transition of $LaAlO_3/SrTiO_3$

Jun Zhou,[1,2,3] Teguh Citra Asmara,[1,2,3] Ming Yang,[1,2,3] George A. Sawatzky,[4] Yuan Ping Feng,[2] and Andrivo Rusydi[1,2,3,*]

[1]*NUSNNI-Nanocore, National University of Singapore, Singapore 117542*

[2]*Department of Physics, National University of Singapore, Singapore 117542*

[3]*Singapore Synchrotron Light Source, National University of Singapore, Singapore 117603*

[4]*Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T1Z1*

(Received 25 May 2014; revised manuscript received 27 June 2015; published 16 September 2015)

The mechanism responsible for the extraordinary interface conductivity of $LaAlO_3$ on $SrTiO_3$ and its insulator-metal transition remains controversial. Here, using density functional theory calculations, we establish a comprehensive and coherent picture that the interplay of electronic reconstructions, lattice distortions, and surface oxygen vacancies fully compensates the polarization potential divergence in $LaAlO_3/SrTiO_3$, explaining naturally the experimental observations under different conditions. While lattice distortions and a charge redistribution between LaO and AlO_2 sublayers play a dominant role in the insulating state, a spontaneous appearance of 1/4 oxygen vacancies per AlO_2 sublayer at the $LaAlO_3$ surface accompanied by $0.5e^-$ charge transfer into the interface is responsible for interface conductivity and the discontinuous transition in $LaAlO_3/SrTiO_3$. Our model also explains properties of $LaAlO_3/SrTiO_3$ prepared with different growth conditions.

DOI: 10.1103/PhysRevB.92.125423 PACS number(s): 71.15.Mb, 73.20.−r, 73.21.−b

PHYSICAL REVIEW B **93**, 155167 (2016)

Tuning polarization states and interface properties of $BaTiO_3/SrTiO_3$ heterostructure by metal capping layers

Jun Zhou,[1,2,3] Ming Yang,[4,5] Lei Shen,[6] Qing Yun Wu,[7] Lei Xu,[2] Yuan Ping Feng,[2,5,*] and Andrivo Rusydi[1,2,3,†]

[1]*NUSNNI-Nanocore, National University of Singapore, Singapore 117542*

[2]*Department of Physics, National University of Singapore, Singapore 117542*

[3]*Singapore Synchrotron Light Source, National University of Singapore, Singapore 117603*

[4]*Institute of Materials Research and Engineering, 2 Fusionopolis Way, Singapore 138634*

[5]*Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore 117546*

[6]*Engineering Science Programme, National University of Singapore, Singapore 117575*

[7]*Department of Materials Science and Engineering, National University of Singapore, Singapore 117575*

(Received 30 December 2015; revised manuscript received 20 March 2016; published 29 April 2016)

How to tune two-dimensional electron gas at interface of heterostructures is becoming an important question for both fundamental physics and electronic applications. Here, using density functional theory calculations, we find that the polarization state of $BaTiO_3$ in metal capped $BaTiO_3/SrTiO_3$ heterostructures changes dramatically, depending on the termination of $BaTiO_3$ and the different metal layers (M = Al, Fe, Pt Au). Most interestingly, for Pt on the BaO-terminated $BaTiO_3/SrTiO_3$, interface conductivity can be tuned. With a paraelectric state in $BaTiO_3$, Pt_$BaTiO_3/SrTiO_3$ remains insulating at interface, while when $BaTiO_3$ is ferroelectric, a hole- or electron-conducting $BaTiO_3/SrTiO_3$ interface can be realized, depending on its polarization direction in $BaTiO_3$. This conducting interface and the top Pt layer screen the depolarization field, and thus stabilize the ferroelectricity in $BaTiO_3$. Our result provides important clues for the reversibly tunable conductivity at oxide interfaces.

DOI: 10.1103/PhysRevB.93.155167