

Controlling band alignments by artificial interface dipoles at perovskite heterointerfaces

Takeaki Yajima^{1,2}, Yasuyuki Hikita¹, Makoto Minohara^{1,3}, Christopher Bell^{1,†}, Julia A.

Mundy⁴, Lena Fitting Kourkoutis⁴, David. A. Muller^{4,5}, Hiroshi Kumigashira⁶,

Masaharu Oshima⁷, and Harold Y. Hwang^{1,3}

¹*Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA*

²*Department of Materials Engineering, The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan*

³*Geballe Laboratory for Advanced Materials, Department of Applied Physics, Stanford University, Stanford, California 94305, USA*

⁴*School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, USA*

⁵*Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA*

⁶*Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan*

Submitted to Nature Communications.

⁷*Department of Applied Chemistry, The University of Tokyo, Bunkyo, Tokyo 113-8656,*

Japan

†*Current Address: H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue,*

Bristol, BS8 1TL, UK

Correspondence and requests for materials should be addressed to T.Y.

(yajima@adam.t.u-tokyo.ac.jp) and H.Y.H. (hyhwang@stanford.edu).

The concept “the interface is the device” is embodied in a wide variety of interfacial electronic phenomena and associated applications in oxide materials, ranging from catalysts and clean energy systems to emerging multifunctional devices. Many device properties are defined by the band alignment, which is often influenced by interface dipoles. On the other hand, the ability to purposefully create and control interface dipoles is a relatively unexplored degree of freedom for perovskite oxides, which should be particularly effective for such ionic materials. Here we demonstrate tuning the band alignment in perovskite metal-semiconductor heterojunctions over a broad range of 1.7 eV. This is achieved by the insertion of positive or negative charges at the interface, and the resultant dipole formed by the induced screening charge. This approach can be broadly used in applications where decoupling the band alignment from the constituent work functions and electron affinities can enhance device functionality.

Introduction

The rich physical properties of oxide interfaces present a formidable challenge, both in terms of scientific opportunities and for device design¹. Several wide gap oxide semiconductors, for example, are candidates for the next-generation of optoelectronic

devices², taking advantage of their transparent nature³. More fundamentally, the discoveries of new electronic phases at oxide heterointerfaces highlight their strongly correlated electronic structure, intertwining charge, spin, and orbital degrees of freedom⁴. Furthermore, oxide interfaces are central constituents in clean energy research, such as in photocatalysis^{5,6} and solar cells⁷. In all of these fields, a common principle which defines the device properties is the band alignment. In the simplest approximation, the band alignment between two materials is determined by the difference in their bulk electron affinities⁸. In reality, forming the interface often triggers the emergence of localized states (e.g., metal-induced gap states), which dominate the band alignment over the electron affinity rule⁹. Oxides are interesting in this regard for a number of reasons. Firstly, for ionic materials the formation of in-gap (localized) interface states is far less likely, in contrast to the dangling bonds often found at covalent systems^{10,11}. Additionally, the recent development of atomic-scale perovskite heterostructures suggests the possibility to design dipole-induced modulations of the potential profile, which are expected to be larger for ions than for bond-centered covalent charge distributions.

In this work, we demonstrate this design possibility using SrRuO₃/Nb:SrTiO₃ perovskite metal/semiconductor Schottky heterojunctions; they are an ideal starting

point in that the experimentally measured Schottky barrier height (SBH) is accurately given by the energy difference between the SrRuO₃ metal work function (Φ) and the Nb:SrTiO₃ n-type semiconductor electron affinity (χ)^{12,13}. Our aim is to insert an artificial interface dipole, by which an additional modulation (Δ) of the potential can be achieved, leading to $\text{SBH} = \Phi - \chi + \Delta$. By using the artificial interface dipole, the SBH at the SrRuO₃/Nb:SrTiO₃ Schottky junction was controlled over a broad range of 1.7 eV. This level of control, representing a change of approximately 50 % of the oxide semiconductor band gap, provides a compelling toolbox for oxide materials in a wide range of applications.

Results

Design of interface dipoles. In the case of Schottky junctions, the artificial interface dipole can be formed in an elegant way: a monolayer of perovskite was inserted, which ionizes to give up an electron/hole which lies close to the layer as screening charge. Thus the dipole is formed by the ionized layer and the transferred electron/hole. For the ionized layers, (LaO)⁺ (Fig. 1a) and (AlO₂)⁻ (Fig. 1b) are created by depositing just a few unit cells (uc) of either LaTiO₃ or SrAlO_x between the SrRuO₃ and Nb:SrTiO₃ (see Methods section). In addition to the original space charge in the Nb:SrTiO₃ and

screening charge in the SrRuO₃, additional ionic charge in the semiconductor and screening charges in the metal are introduced (Figs. 1c and d), forming a large atomic-scale electric dipole at the interface (Figs. 1e and f). This dipole modifies the band diagram according to its direction, and the resulting SBH (and Δ) can easily be detected by a host of well-established techniques. In this article,

Electrical characterizations of SBHs. Figures 2a and b show the current-voltage (I - V) characteristics for SrRuO₃/Nb:SrTiO₃ Schottky junctions with various (LaO)⁺ and (AlO₂)⁻ layer coverage. The increase in forward bias current by (LaO)⁺ layer insertion (Fig. 2a) indicates the reduction of the SBH. A complete monolayer of (LaO)⁺ triggered a total collapse of the SBH, creating an Ohmic contact (Fig. 2a inset). In the case of (AlO₂)⁻ layer insertion, the SBH is enhanced, as inferred from the suppression of the current for a given voltage as the ionic charge layer increases (Fig. 2b). For all samples, $\log|I|$ vs. V is linear under forward bias, indicating transport via thermionic emission¹⁴ (Fig. 2b inset). From the intercept of extrapolating the forward bias region, the deduced SBH decreased from 1.4 eV to 0.7 eV after the insertion of 0.6 uc (LaO)⁺ layer, while with 2 uc of (AlO₂)⁻, it increased to 1.9 eV. Here, it should be noted that above 0.6 uc (LaO)⁺ layer, the SBH is too low to be evaluated by electrical measurements. We also note that all junctions, even in cases of fractional layer insertion, showed ideal

rectification with ideality factors near unity. This is reasonable since from atomic force microscopy, the characteristic lateral scale of the inhomogeneity in the fractional layers (< 10 nm), is far smaller than the depletion width of the junctions (~ 100 nm), such that the barrier heights are smoothed out microscopically and maintain a uniform electrostatic potential profile across the heterointerface^{15,16}.

These SBH changes were confirmed by capacitance-voltage (C - V) measurements, as shown in Figs. 2c and d. All the junctions showed the characteristic linear relationship¹⁴ between $1/C^2$ and V (Fig. 2d inset). In this case, the abscissa intercept of the linear extrapolation corresponds to the built-in potential of these junctions, which is approximately 0.1 eV smaller than the SBH at this doping density. Again we found a large decrease in the SBH (from 1.3 eV to 0.7 eV) with 0.6 uc (LaO)⁺ layer insertion, and a correspondingly large increase (to 1.8 eV) with 2 uc of (AlO_2)⁻ layer insertion. Above 0.6 uc of (LaO)⁺ layer, the C - V data were no longer reliable because of the low impedance of the junctions.

Spectroscopic characterizations of SBHs. In addition to the electrical measurements, direct zero bias SBH measurements were performed using internal photoemission spectroscopy¹⁴ (IPE) and x-ray photoemission spectroscopy¹² (PES). In IPE, photoexcited electrons on the metallic side traverse the interface and are detected as a

photocurrent (Fig. 3a inset). The SBH corresponds to the extrapolated onset energy of the square root of the photoyield, (the photocurrent per incident photon)¹⁷. IPE spectra for all the SrRuO₃/Nb:SrTiO₃ Schottky junctions with (LaO)⁺ and (AlO₂)⁻ layer insertions are plotted in Fig. 3a. From these data we find that the SBH decreased from 1.4 eV to 1.0 eV for a (LaO)⁺ layer of 0.6 μc , and increased to 1.7 eV with 2 μc of (AlO₂)⁻ layer, in quantitative agreement with the electrical measurements. Furthermore, three representative samples were measured with PES, using the Ti 2*p*_{3/2} core level shift with respect to the Fermi level E_F (Fig. 3b inset), providing a direct measure of the built-in potential^{12,18}. As shown in Fig. 3b, it is qualitatively clear that the binding energy of the Ti 2*p*_{3/2} core level shifts to higher/lower energies when (LaO)⁺/(AlO₂)⁻ layer is inserted, consistent with a decrease/increase in the SBH. More quantitatively, the PES spectra were decomposed into Ru 3*p*_{3/2} and Ti 2*p*_{3/2} components. The SBH shift was then obtained from the difference in the peak energies, after normalization to the 1.3 eV SBH value of the reference SrRuO₃/Nb:SrTiO₃ junction. These data, along with the values obtained from *I-V*, *C-V* and IPE, are plotted as a function of the interlayer in Fig. 4a. All four methods show good quantitative agreement, experimentally demonstrating proposed SBH tuning.

Direct observations of the interfacial atomic structures. Of course, the real systems

are not perfectly ideal; cross-section scanning transmission electron microscopy (STEM) images are given for the end-member interfaces (Fig. 4b and c). While La ions showed an atomically flat interlayer in Fig. 4b, Al ions sometimes formed patches as shown in Fig. 4c. Details of the growth of $(\text{LaO})^+$ and $(\text{AlO}_2)^-$ insertion layers are given elsewhere^{19,20}. The aspect most relevant here is that the SrAlO_x used for $(\text{AlO}_2)^-$ insertion is not a stable perovskite in bulk, and can only be stabilized in thin layers using epitaxial strain²⁰. It is likely that the intended $(\text{AlO}_2)^-$ layer is not completely oxidized even after the post-annealing (see Methods section), possibly reflecting the recently discussed electrostatic stabilization of charged defects at oxide interfaces or surfaces²¹, resulting in the overall asymmetry of Fig. 4a and the apparent saturation of Schottky barrier shifts above a single layer thickness.

Discussion

The dipole formation by $(\text{LaO})^+$ insertion layer is reminiscent of the formation of two dimensional electron gas by $(\text{LaO})^+$ insertion in the SrTiO_3 matrix^{19,22}. In this case, the replacement of La with Sm or Y may localize the electrons by forming a split-off lower Hubbard band a few hundred meV below the conduction band edge. However, in a Schottky junction, these localized electrons can be depleted in the Schottky barrier with

the SBH of the order of 1eV. Therefore, we predict that many other rare earth oxide layers including (SmO)⁺ and (YO)⁺ may also decrease the SBH in the same way as the (LaO)⁺ layer.

The total tunable range of ~1.7 eV is remarkably large compared with other materials systems such as organics^{23,24} and conventional semiconductors²⁵⁻²⁷, where the magnitude of the interface dipole by self-assembled monolayers and highly-doped interlayers are limited by overlayer effects and small dopant solubility. The high efficiency of dipole engineering in oxide heterostructures demonstrated here originates from their ionic character as well as electronic and structural flexibility. Given such characteristics, oxide heterostructures represent an excellent platform where the band alignments are freely controlled by nano-scale interface engineering. This approach can be broadly applied to designing electrical contacts, interfaces optimized for charge separation, and band lineups with respect to redox potentials, further expanding the functionality of this versatile class of materials.

Methods

Device fabrication. The Schottky junctions were fabricated by pulsed laser deposition using TiO₂-terminated Nb:SrTiO₃ (001) substrates (Nb = 0.01 wt%). LaTiO₃ (0-1 uc)

was grown at an O₂ pressure of 10⁻⁵ Torr, while SrAlO_x (0-2 uc) and SrRuO₃ (40 uc) were grown at 0.3 Torr. The substrate temperature was 750 °C in all cases. The thicknesses were controlled by using reflection high-energy electron diffraction oscillations and X-ray reflectivity. For Ohmic contacts, gold was evaporated onto the SrRuO₃, and the whole structure was Ar-ion etched to form the junction area of 0.091 mm². Post-annealing was performed in 760 Torr O₂ at 300 ~ 350 °C for 6 hours to fill oxygen vacancies introduced by Ar-ion etching as well as originally existing in the SrAlO_x. Although SrAlO_x is not a stable bulk perovskite, epitaxial stabilization is possible in an ultra-thin layer²⁰, and by filling oxygen vacancies, we can ideally form negatively charged (AlO₂)⁻ layer.

SBH measurements. In the SBH estimate from *I-V* characteristics, the small deviation of the ideality factor (*n*) from unity was compensated by taking the intercept of the linear extrapolation between the measured SBH and *n* (Ref. 16). The PES measurements using synchrotron radiation were carried out on beamline BL2C at the Photon Factory in KEK, Japan, with 800 eV incident photon energy. The PES spectra were recorded using a Scienta SES-2002 electron energy analyzer with a total energy resolution of 150 meV. For the PES experiments, 2 nm thick SrRuO₃ films were used to minimize the attenuation of the emitted photoelectrons, and reduce the effect of the overlapping Ti

$2p_{2/3}$ and Ru $3p_{2/3}$ core-level spectra. We confirmed that for this thinner SrRuO₃, the electric properties were essentially unchanged.

STEM. STEM of cross sectional samples was performed by high-angle annular dark field (HAADF) imaging in an FEI Tecnai F20-ST.

References

1. Kroemer, H. Quasi-electric fields and band offsets: teaching electrons new tricks.
http://nobelprize.org/nobel_prizes/physics/laureates/2000/kroemer-lecture.html
(2000).
2. Tsukazaki, A. *et al.* Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO. *Nature Mater.* **4**, 42-46 (2005).
3. Nomura, K. *et al.* Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* **432**, 488-492 (2004).
4. Hwang, H. Y. *et al.* Emergent phenomena at oxide interfaces. *Nature Mater.* **11**, 103-113 (2012).
5. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**, 37-38 (1972).
6. Kato, H., Asakura, K. & Kudo, A. Highly efficient water splitting into H₂ and O₂

- over lanthanum-doped photocatalysts with high crystallinity and surface nanostructure. *J. Am. Chem. Soc.* **125**, 3082-3089 (2003).
7. O'Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **353**, 737-740 (1991).
 8. Anderson, R. L. Experiments on Ge-GaAs heterojunctions. *Solid-State Electron.* **5**, 341-351 (1962).
 9. Cowley, A. M. & Sze, S. M. Surface states and barrier height of metal-semiconductor systems. *J. Appl. Phys.* **36**, 3212-3220 (1965).
 10. Kurtin, S., McGill, T. C. & Mead, C. A. Fundamental transition in the electronic nature of solids. *Phys. Rev. Lett.* **22**, 1433-1436 (1969).
 11. Dong, Y. F., Mi, Y. Y., Feng, Y. P., Huan, A. C. H. & Wang, S. J. *Ab initio* studies on Schottky barrier heights at metal gate/LaAlO₃ (001) interfaces. *Appl. Phys. Lett.* **89**, 122115 (2006).
 12. Minohara, M., Ohkubo, I., Kumigashira, H. & Oshima, M. Band diagrams of spin tunneling junctions La_{0.6}Sr_{0.4}MnO₃/Nb:SrTiO₃ and SrRuO₃/Nb:SrTiO₃ determined by *in situ* photoemission spectroscopy. *Appl. Phys. Lett.* **90**, 132123 (2007).
 13. Hikita, Y., Kozuka, Y., Susaki, T., Takagi, H. & Hwang, H. Y. Characterization of the Schottky barrier in SrRuO₃/Nb:SrTiO₃ junctions. *Appl. Phys. Lett.* **90**, 143507

(2007).

14. Sze, S. M. & Ng, K. K. *Physics of semiconductor devices*, 3rd edn (John Wiley & Sons, Hoboken, 2007).
15. Tung, R. T. Electron transport of inhomogeneous Schottky barrier. *Appl. Phys. Lett.* **58**, 2821-2823 (1991).
16. Sullivan, J. P., Tung, R. T., Pinto, M. R. & Graham, W. R. Electron transport of inhomogeneous Schottky barrier: A numerical study. *J. Appl. Phys.* **70**, 7403-7424 (1991).
17. Fowler, R. H. The analysis of photoelectric sensitivity curves for clean metals at various temperatures. *Phys. Rev.* **38**, 45-56 (1931).
18. Niles, D. W., Margaritondo, G., Perfetti, P., Quaresima, C. & Capozzi, M. Heterojunction band discontinuity control by ultrathin intralayers. *Appl. Phys. Lett.* **47**, 1092-1094 (1985).
19. Ohtomo, A., Muller, D. A., Grazul, J. L. & Hwang, H. Y. Artificial charge-modulation in atomic-scale perovskite titanate superlattices. *Nature* **419**, 378-380 (2002).
20. Sato, H. K. *et al.* Nanometer-scale epitaxial strain release in perovskite heterostructures using “SrAlO_x” sliding buffer layers. *Appl. Phys. Lett.* **98**, 171901

(2011).

21. Yu, Y. & Zunger, A. A unifying mechanism for conductivity and magnetism at interfaces of insulating nonmagnetic oxides. *Nat. Commun.* **5**, 5118 (2014).
22. Jang, H. W. *et al.* Metallic and insulating oxide interfaces controlled by electronic correlations. *Science* **331**, 886-889 (2011).
23. Campbell, I. H. *et al.* Controlling charge injection in organic electronic devices using self-assembled monolayers. *Appl. Phys. Lett.* **71**, 3528-3530 (1997).
24. Marmont, P. *et al.* Improving charge injection in organic thin-film transistors with thiol-based self-assembled monolayers. *Org. Electron.* **9**, 419-424 (2008).
25. Shannon, J. M. Control of Schottky barrier height using highly doped surface layers. *Solid-State Electron.* **19**, 537-543 (1976).
26. Han, C. C. *et al.* Barrier height modification of metal/germanium Schottky diodes. *J. Vac. Sci. Technol. B* **6**, 1662-1666 (1988).
27. Koyanagi, K., Kasai, S. & Hasegawa, H. Control of GaAs Schottky barrier height by ultrathin molecular beam epitaxy Si interface control layer. *Jpn. J. Appl. Phys.* **32**, 502-510 (1993).

Acknowledgements We acknowledge experimental support from M. Lippmaa, R.

Takahashi, K. Nishio, T. Harada, S. Toyoda, and T. Namiki. We acknowledge support from the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract DE - AC02 - 76SF00515 (T.Y., Y.H., M.M., C.B., & H.Y.H.). T.Y. also acknowledges support from the Japan Society for the Promotion of Science (JSPS).

Author Contributions T.Y. performed the device fabrication, measurements, and data analysis. Y.H., C.B., and H.Y.H. assisted with the planning, measurements, and analysis of the study. M.M., H.K., and M.O. supported the PES measurements and analysis, and J.A.M, L.F.K, and D.A.M. performed the electron microscopy.

Reprints and permissions information is available at www.nature.com/reprints.

Competing interests statement The authors declare that they have no competing financial interests.

Figure Captions:

Figure 1 | Interface dipole engineering at perovskite Schottky junctions. a, b,

Schematics of ionic alignments at SrRuO₃/Nb:SrTiO₃ heterointerfaces with (LaO)⁺ and (AlO₂)⁻ layer insertion. As a function of distance from each heterointerface, **c**, **d**, the charge distributions and **e**, **f**, the electronic band diagrams are shown. The interface dipole between the ionic charge and the induced screening charge **e**, decreases or **f**, increases the SBH, both maintaining the relationship: $SBH = \Phi - \chi + \Delta$. E_{vac} , E_C , and E_F denote the vacuum level, the conduction band edge in Nb:SrTiO₃, and the Fermi level of the whole system.

Figure 2 | Electrical measurements of the SBH. **a**, **b**, $\log|I|$ - V plots for SrRuO₃/Nb:SrTiO₃ Schottky junctions (0.091 mm²) with inserted (LaO)⁺ and (AlO₂)⁻ layers respectively. Inset in **a** shows the linear plot for the junction with 1 uc (LaO)⁺ layer insertion. **c**, **d**, $1/C^2$ - V plots for SrRuO₃/Nb:SrTiO₃ Schottky junctions with inserted (LaO)⁺ and (AlO₂)⁻ layers. The amount of (LaO)⁺ and (AlO₂)⁻ was varied from 0 uc to 1 uc (**a** and **c**) and from 0 uc to 2 uc (**b** and **d**), respectively. Insets in **b** and **d** show schematic band diagrams for each measurement. For the latter, ϵ_s , W , and V_{bi} denote the semiconductor permittivity, the depletion width, and the built-in potential.

Figure 3 | Photoelectric measurements of the SBH. **a**, **b**, IPE and PES spectra for

SrRuO₃/Nb:SrTiO₃ Schottky junctions with (LaO)⁺ and (AlO₂)⁻ insertions. Red lines in **a** show the region over which the linear extrapolation (dashed lines) was carried out. Insets show the schematics of each measurement. The black arrow in **b** represents the detection width (~ 1 nm).

Figure 4 | Summary of the SBH tuning. **a**, SBH values obtained from *I-V*, *C-V*, IPE, and PES measurements plotted as a function of interlayers, (LaO)⁺ and (AlO₂)⁻. **b**, **c**, HAADF-STEM images of SrRuO₃/Nb:SrTiO₃ heterointerfaces with **b**, 1 uc (LaO)⁺ and **c**, 2 uc (AlO₂)⁻ insertions.







