

論文の内容の要旨

論文題目 Artificial Interface Dipoles at Oxide Heterointerfaces:

Fundamentals and Devices

(酸化物ヘテロ界面における界面ダイポールの設計とデバイス応用)

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Introduction

Perovskite oxides (with the crystal structure ABO_3 , as shown in Fig. 1a) are characterized by a wide diversity of physical properties originating from the electronic d -orbitals, ranging from strong electronic correlation effects to catalytic behavior. Crucially this crystal structure, supported by an oxygen framework, is robust against ionic substitution, enabling these diverse physical properties to be incorporated in epitaxial heterostructures. Perovskite heterointerfaces and surfaces have shown exotic electronic phases and device functionalities, including two-dimensional electronic states, magnetic Schottky junctions, and artificial multiferroics. In this context, it is important to note that the electrostatic description of a heterointerface has only two boundary parameters: an interface charge and an interface dipole. While the former, causing interfacial electronic depletion or accumulation, is widely used to create novel interface physics, the latter, modifying the interfacial band offset by an electrostatic dipole on the atomic scale (Fig. 1b and c), has not been fully investigated in perovskite heterostructures. This is due to a combination of the relatively complex concept, as well as the difficulties of experimentally evaluating the accurate band diagram. This thesis presents a systematic study of engineering interface dipoles at perovskite oxide heterointerfaces, dealing with both fundamental aspects, and device applications. Although such dipole engineering has been a longstanding problem in conventional semiconductors, here a sizable but well-controlled interface dipole is demonstrated using an ionic charge layer, which is readily incorporated in perovskite heterostructures. Because the design of interfacial electronic phases and devices are based on the interfacial band alignment, the ability to arbitrarily control band offsets using interface dipoles can be extremely powerful for both pure and applied oxide research.

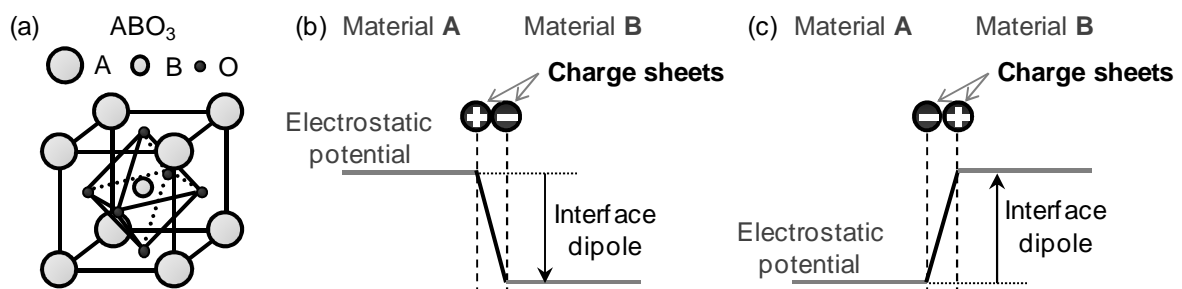


Fig. 1 Schematic illustrations of (a) a perovskite structure, ABO_3 , and (b, c) electrostatic interface dipoles, decreasing and increasing respectively, the electrostatic potential from Material A to B.

Theoretical background

The conceptual complexity of the surface or interface dipole comes from the fact that its *absolute*

magnitude cannot be simply extracted from a measurement of the work function of the bulk materials. In a given system, by systematically changing the interface structure, only *relative* changes in the interface dipole can be measured. This restriction stems from the need to consider the electrostatic boundary conditions on an atomic scale. While first principle calculations have succeeded in extracting the *absolute* magnitude of the interface dipole¹, reproducing the interfacial discontinuity of core level energies in photoemission spectra, a more generalized theoretical framework is needed to address the universality of this issue. Here we discuss the most generalized form for the *absolute* magnitude of the interface dipole, providing a conceptual foothold for the discussion of interface dipole engineering in perovskite heterostructures.

The interface dipole is defined as the difference of the electrostatic potential standard in each material constituting the interface. Although this potential standard is usually defined for a given material with respect to the vacuum at infinity, the existence of a surface dipole modifies the electrostatic potential in the materials, making this definition defunct. Here, starting from the Green's function of the Poisson's equation, $q/4\pi\epsilon_0 r$ (q : charge, ϵ_0 : vacuum permittivity, r : distance from the charge), the potential standard at vacuum infinity is recalculated as the average electrostatic potential in each local unit cell (uc). This defines the electrostatic potential standard in a material, reflecting the interface dipole, but not the periodic potential variation on the atomic scale. The interface dipole (Δ) is calculated as:

$$\Delta = \frac{-e}{\epsilon_0} \left[(Q_{zz}^{A'} - Q_{zz}^{B'}) + \int_{z_1}^{z_2} \rho'(z) z \mathbf{d}z \right],$$

$$\rho'(z) = \rho(z) + [P_z^A \delta(z - z_1) - P_z^B \delta(z - z_2)].$$

e is the elementary charge, and $Q_{zz}^{A'}$ (P_z^A) and $Q_{zz}^{B'}$ (P_z^B) are the zz (z) component of the quadrupole (dipole) moment density in the unit cell of each material.

$\rho'(z)$, describes the overall interface charge, where the first term, $\rho(z)$, is the microscopic charge density in the interface region arbitrarily defined between $z = z_1$ and $z = z_2$, and the second term is the contribution from the polarization in each material. The first and second term in Δ is the interface dipole from the quadrupole moment in each material and that from $\rho'(z)$, respectively (Fig. 2). Δ , thus calculated, is invariant to arbitrary definitions of the interface region (z_1 and z_2) or the unit cell in each material, but at the same time, clearly shows the physical origin of the interface dipole. In the following experiments of the interface dipole engineering, we designed the term of $\rho(z)$ at perovskite oxide heterointerfaces, as is also the case for the interface dipole engineering in conventional semiconductors.

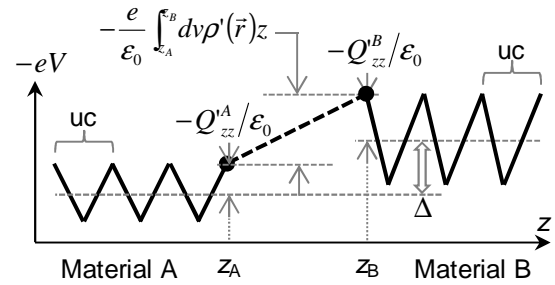


Fig. 2 A schematic illustration of an interface dipole. V denotes the electrostatic potential.

Demonstration

A Schottky junction, formed between a metal and a semiconductor, is defined by the Schottky barrier height, $SBH = W - \chi + \Delta$ (W : metal work function, χ : semiconductor electron affinity). Since SBH can be measured in a variety of ways, this junction provides a device platform for studying the control of Δ . Historically, in Schottky junctions formed with covalent semiconductors, SBH is almost independent of W due to an Δ caused by unintended interface charges. Ionic semiconductors, such as the oxides, tend to mitigate this problem², facilitating Δ as a controllable degree of freedom at heterointerfaces. In the following experiments, Δ was tuned in Schottky junctions using perovskite oxide by inserting an ionic charge sheet at a heterointerface. This charge sheet induces a counter screening charge in the metal, creating the Δ required to shift the SBH (Fig. 3a).

The Schottky junctions were fabricated by pulsed laser deposition (PLD), growing SrRuO₃, a readily available oxide with good metallicity, on {100} Nb-doped SrTiO₃, a widely used N-type oxide semiconductor. A highly concentrated laser beam ablates the target material and deposits it onto a heated substrate to grow a single crystal thin film. Monitoring the diffraction intensity of an electron beam grazing the surface enables us to control the film thickness at an atomic level during growth. 0-2 uc of LaTiO₃ or SrAlO_x were grown prior to SrRuO₃, introducing (LaO)⁺ or (AlO₂)⁻ ionic charges at the SrRuO₃/Nb:SrTiO₃ heterointerface. This insertion was confirmed by scanning transmission electron microscope (STEM) images as shown in Fig. 3b. The magnitude of the shift of the SBH due to Δ was evaluated through current-voltage (*IV*), capacitance-voltage (*CV*), internal photoemission (IPE), and X-ray photoemission (PES) measurements.

Fig. 4a shows PES spectra of Ti 2*p*_{3/2} core levels in 1 uc (LaO)⁺-inserted, non-inserted, and 2 uc (AlO₂)⁻-inserted Schottky junctions, plotting the photoemission intensity as a function of the binding energy with respect to the Fermi level. Because the shift of the Ti 2*p*_{3/2} core level peak reflects changes in Δ , a shift to higher binding energy by (LaO)⁺ insertion means a smaller SBH, and vice versa for (AlO₂)⁻. The SBHs from all the four measurements are summarized in Fig. 4b, showing an evolution from 0 eV to 1.7 eV by (LaO)⁺ or (AlO₂)⁻ insertion with respect to the original SBH of 1.2 eV for no insertion. This magnitude of Δ is remarkable with respect to conventional semiconductors, highlighting the advantage of perovskite heterostructures. Δ was also controlled in a range of other heterointerfaces: SrRuO₃/LaAlO₃/Nb:SrTiO₃, La_{0.5}Sr_{0.5}TiO₃/SrAlO_x/Nb:SrTiO₃, and La_{0.7}Sr_{0.3}MnO₃/SrMnO₃/Nb:SrTiO₃, where fundamental issues such as the effects of in-plane inhomogeneity, surface charges, interfacial charged defects, and the interface termination were addressed.

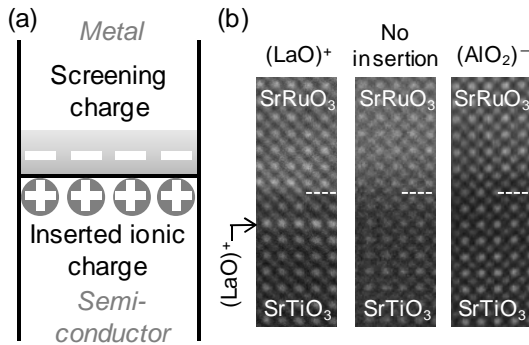


Fig. 3 (a) A schematic illustration of a Schottky junction with interface dipoles between the inserted ionic charge and the counter screening charge. (b) A STEM images of 1 uc (LaO)⁺-inserted, non-inserted, and 2 uc (AlO₂)⁻-inserted SrRuO₃/Nb:SrTiO₃.

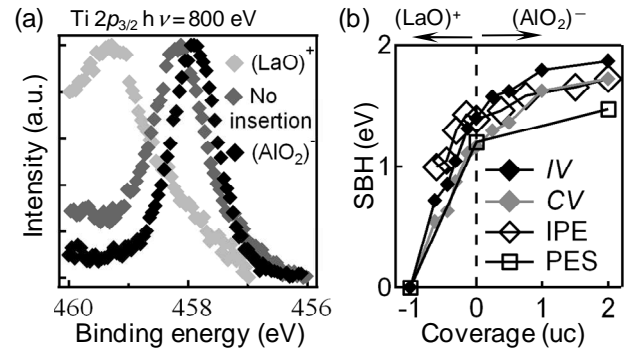


Fig. 4 (a) PES spectra of Ti 2*p*_{3/2} core levels in 1 uc (LaO)⁺-inserted, non-inserted, and 2 uc (AlO₂)⁻-inserted SrRuO₃/Nb:SrTiO₃ Schottky junctions. (b) A SBH plot as a function of inserted layers by four measurements: *IV*, *CV*, IPE, and PES.

Device application

A fundamental application of artificial interface dipole engineering is the controlled creation of Ohmic or rectifying interfaces. In particular, having a highly rectifying (insulating) interface is a key issue in transistors, in which the current channel should be electrically isolated from the control electrodes. A hot electron transistor (HET)³ has a tri-layer structure of semiconductor(emitter)/metal(base)/semiconductor(collector) as shown in Fig. 5a. Hot electrons are ballistically transferred from the emitter to the collector, and can be controlled by the base current. By incorporating ferromagnetic or ferroelectric oxides, multifunctional transistors can be expected, and moreover, the hot electron mean free path (MFP), extracted from this device, provides the direct measure of strong electronic correlation in transition metal oxides.

HETs with a heterostructure of {100} SrTiO₃/La_{0.7}Sr_{0.3}MnO₃/Nb:SrTiO₃ were fabricated, where a ferromagnetic metallic La_{0.7}Sr_{0.3}MnO₃ was chosen for possible magnetic functionalities. Because the transistor characteristics are defined by the emitter current, we must suppress the collector/base leakage current, namely

the reverse bias current in the collector/base Schottky junction. In the as-grown device, however, this leakage current (black arrow in Fig. 5b) was as large as the emitter current (grey arrow), prohibiting the transistor operation. An interface dipole was induced by inserting 1 uc of SrMnO₃, to increase the collector/base SBH, successfully suppressing the leakage current by five orders of magnitude (black arrow in Fig. 5c). Fig. 6 shows the common emitter output characteristics at room temperature, which shows the clear modulation of the collector current by the base current.

However, the device properties fluctuated due to the stochastic existence of pinholes through the base layer. These pinholes can be mitigated by using a scanning probe tip as a nanoscale emitter as shown in Fig. 7a. This approach, known as ballistic electron emission microscopy (BEEM), enhanced the reproducibility of the device properties, making it possible to achieve hot electron spectroscopy. Fig. 7b shows the collector current (transmission current) as a function of the emitter probe bias, which was increased by decreasing temperature, possibly reflecting the spin scattering in La_{0.7}Sr_{0.3}MnO₃.

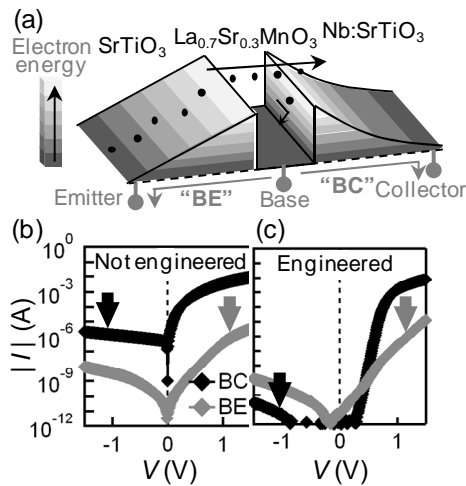


Fig. 5 (a) A schematic band diagram of a SrTiO₃/La_{0.7}Sr_{0.3}MnO₃/Nb:SrTiO₃ HET. IV characteristics of the base/collector (BC) and the base/emitter (BE) Schottky junctions (b) without and (c) with BC interface dipole.

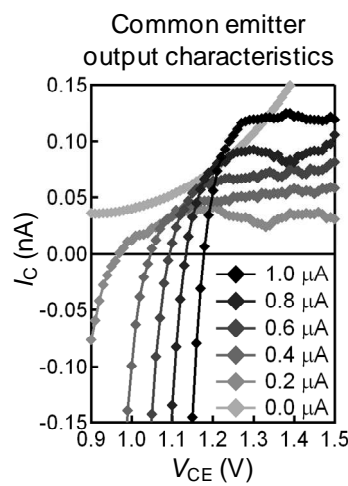


Fig. 6 Room-temperature common emitter output characteristics of the HET, with the fixed base current varied from 0 to 1 μ A.

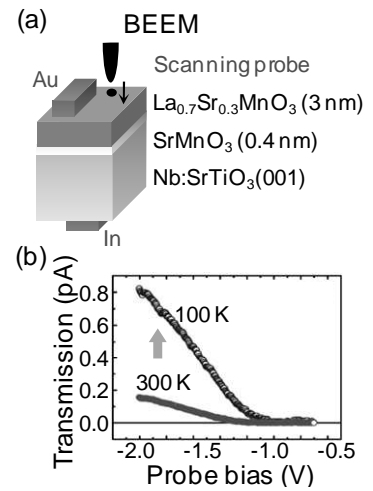


Fig. 7 (a) A schematic illustration of BEEM. (b) Transmission current versus bias from BEEM for different temperatures.

Conclusion

A systematic study of interface dipole engineering at perovskite oxide heterointerfaces was performed, addressing both fundamental issues and the device applications. Firstly, the conceptual groundwork for the interface dipole was presented, calculating its *absolute* magnitude in a general form, invariant to the arbitrary definition of the interface region. Secondly, artificial interface dipoles were demonstrated in {100} SrRuO₃/Nb:SrTiO₃ Schottky junctions with (LaO)⁺ or (AlO₂)⁻ ionic charges inserted, as well as in several other heterointerfaces. The interface dipole was evaluated via four different measurements: IV , CV , IPE, and PES, showing the arbitrary band offset control over a range of up to 1.7 eV. Fundamental issues including the effects of in-plane inhomogeneity, surface charges, interfacial charged defects, and the interface termination were experimentally investigated, elucidating a methodology for the continuous control and the maximization of the interface dipole. Finally, this technique was applied to the fabrication of HETs, establishing a device platform for hot electron spectroscopy in strongly correlated electronic systems, highlighting the power of interfacial dipole engineering in oxide electronics, which cannot be fully exploited in other materials systems.

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