CONTROLLING BAND ALIGNMENTS BY ENGINEERING INTERFACE DIPOLES AT OXIDE HETEROINTERFACES

Takeaki Yajima, Yasuyuki Hikita, Christopher Bell, and Harold Y. Hwang

Department of Advanced Materials Science, Univ. of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.

Introduction

Devices such as dye-sensitized solar cells, batteries, and solid-state electronic devices take advantage of interface electron transfer, in which interface dipoles (electric double layers) play an essential role. Although the functionality of these devices could be greatly enhanced by optimizing the magnitude of the dipoles at the dye/semiconductor interface, the electrode/electrolyte interface, or the solid/solid interface, dipole engineering is often problematic. For example, attempts to engineer the dipole at conventional metal/semiconductor interfaces, which form Schottky junctions, one of the most fundamental elements in electronics, are hindered by the presence of broken covalent bonds at the edge of the semiconductor. These dangling bonds create interface states, pinning the interface chemical potential, and partially canceling out the interface dipole [1].

Ionic materials, on the other hand, are sometimes free from this pinning effect [2], facilitating the formation of dipoles simply by the accurate positioning of the required charges, one after another. Here, in oxides with strong ionic character, we succeeded in creating a huge electric dipole of the order of 1 eV by fabricating an artificial alignment of ions at a metal/semiconductor interface. By varying the sign and number of embedded ions, the direction and magnitude of the interface dipole was tuned in the range -1.17 eV to 0.55 eV, as reflected in a systematic variation of the electric properties of the Schottky junctions. These results demonstrate the validity for using the ionic limit to model dipole engineering in oxides, and imply a larger freedom for structures in devices with ionic materials.

Experimental

Previously, we succeeded in tuning the Schottky barrier height (SBH) in (001)-oriented $La_{0.7}Sr_{0.3}MnO_3$/ $Nb:SrTiO_3$ junctions by up to 0.5 eV, by engineering the interface dipole [3]. In this paper, the (001)-oriented $SrRuO_3/Nb:SrTiO_3$ junction was chosen as the model interface to tune the SBH using interface dipole control. The interface dipole was fabricated by inserting $LaTiO_3$ or $SrAlO_3$ at the interface (Fig. 1a and b). This inserted layer acts as a sheet charge: $(La^{3+}Ti^{4+}O^{2-}_3)^+$ or $(Sr^{2+}Al^{3+}O^{2-}_3)^-$ to form a dipole (or electric double layers) with the counter (screening) charge in the metal $SrRuO_3$ (Fig. 1c and d). These interface dipoles create electrostatic potential offsets (Fig. 1e and f), which modify the SBHs (Fig. 1g and h).

The structures were fabricated by pulsed laser deposition at 750 °C using TiO_2-terminated 0.01 wt. % $Nb:SrTiO_3$ (001) substrates. The oxygen pressure and laser fluences were 0.3 Torr, and 1 J/cm² for $SrRuO_3$, 1 × 10^{-5} Torr, and 0.6 J/cm² for $LaTiO_3$, and 1 × 10^{-3} Torr, and 0.8 J/cm² for $SrAlO_3$. After the $LaTiO_3$ or $SrAlO_3$ interlayer growth, 60 unit cells (uc) of $SrRuO_3$ was then deposited. The interlayer thickness was varied from 0 uc to 1 uc for $LaTiO_3$, and from 0 uc to 2 uc for $SrAlO_3$. In order to eliminate oxygen vacancies which can reduce the inserted negative charges by forming $(SrAlO_{3-\delta})^{-(1-\delta)}$, all of the structures incorporating $SrAlO_3$ were post-annealed in flowing O_2 at 800 °C for 4 hours. Precise control of the interlayer thickness was achieved by *in-situ* monitoring of the reflection high-energy electron diffraction intensity and the laser pulse number with feedback from the surface morphology as measured *ex-situ* by atomic force microscopy. The SBH was evaluated from current – voltage characteristics, capacitance – voltage characteristics, and internal photoemission spectra.
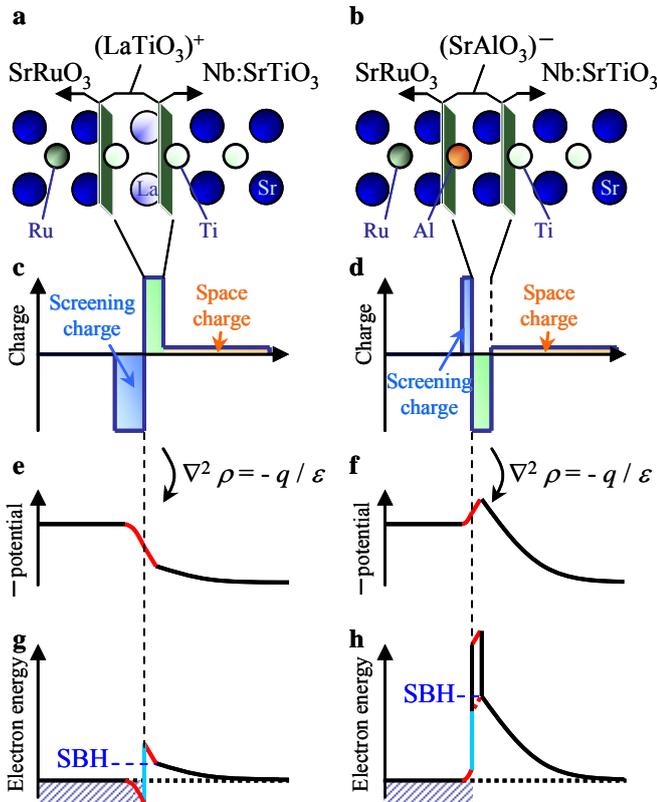

Fig. 1. Schematic illustrations of two types of interface dipoles, $SrRuO_3/LaTiO_3$ and $SrRuO_3/SrAlO_3$, on $Nb:SrTiO_3$ (001) substrates. **a**, **b**, Schematics of the atomic arrangements. **c**, **d**, Charge profiles. **e**, **f**, (Negative) potential profiles. **g**, **h**, Band diagrams. Gauss's law is indicated in **e** and **f**.
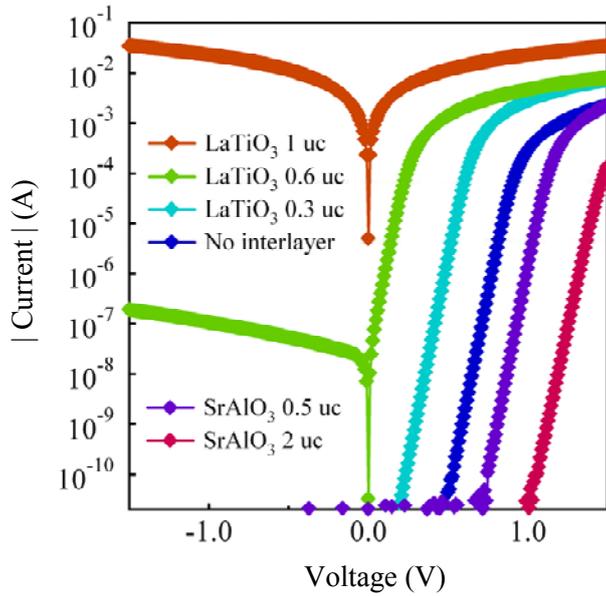
Fig. 2. Current-voltage characteristics of (001)-oriented SrRuO₃/Nb:SrTiO₃ Schottky junctions with various thicknesses of an LaTiO₃ or SrAlO₃ inserted dipole layer.
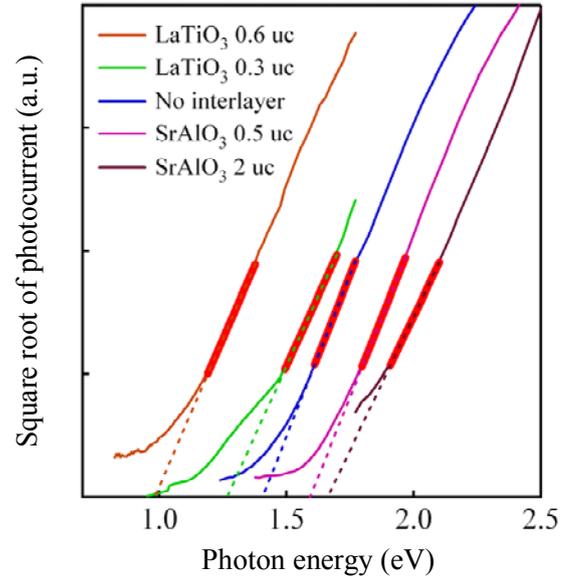

Fig. 3. Internal photoemission spectra of (001)-oriented SrRuO₃/Nb:SrTiO₃ Schottky junctions with various thicknesses of an LaTiO₃ or SrAlO₃ inserted dipole layer. The broken lines are linear extrapolations of the spectra in the range indicated by the thick red lines.

Results and discussion

As shown in Fig. 2, the current-voltage characteristics could be varied from Ohmic to rectifying with a 1.72 eV barrier height, reflecting the SBH tuning by the interface dipole from the original SrRuO₃/Nb:SrTiO₃ junction, where the SBH was 1.17 eV. The sign of the interface dipole was consistent with the schematics shown in Fig. 1: the SBH was reduced using LaTiO₃ insertion, and increased using SrAlO₃. The rectifying properties were well described by the thermionic emission model, with ideality factors close to unity. This systematic shift in the SBHs was also observed both in the capacitance – voltage characteristics, and the internal photoemission data (Fig. 3). For the latter measurements, all of the spectra showed a linear relationship between the square root of photocurrent yield and the photon energy [4], and the SBH was obtained by extrapolation of this linear region as indicated by broken lines in Fig. 3.

Conclusion

Dipole engineering was demonstrated using SrRuO₃/Nb:SrTiO₃ Schottky junctions, taking advantage of the ionic character of these oxides. The SBH, originally 1.17 eV, was tuned using the interface dipole in a broad range from 0 eV to 1.72 eV, as measured using current – voltage characteristics, capacitance – voltage characteristics, and internal photoemission spectra. In a simple electrostatic picture, these interface dipoles can be understood to be formed by the inserted $(La^{3+}Ti^{4+}O^{2-}_3)^+$ or $(Sr^{2+}Al^{3+}O^{2-}_3)^-$ sheet charges and the counter (screening) charge in the metal SrRuO₃. Engineering interface dipoles in this manner has

enormous potential for controlling the band alignments of junctions used in oxide electronics, as well as for improving the functionality of dye-sensitized solar cells and batteries.

References

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