**Engineering Artificial Interface Dipoles at Oxide Heterointerfaces**

In all contemporary electronic devices, the most fundamental design constraint is the band alignment between two materials at a heterointerface. A central focus of a wide range of fields and various disciplines is therefore the control of such energy bands to enhance the properties without affecting the bulk properties of the materials. While the insertion of interface charges has been utilized to control band offsets in conventional semiconductors and organic materials, here we show that the ionic nature of the complex oxides can be used to vastly enhance the degree and magnitude of band offset control. As a general experimental proof of principle, we use atomically controlled layers of positive and negative charge at a well-defined oxide metal/semiconductor Schottky junction to produce an interface dipole that varies the barrier height over a range of 1.7 eV. This large control — representing a change of over 50% of the oxide semiconductor band gap — provides a compelling new tool for complex oxides in a wide range of applications.

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, 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 band alignment at this interface was tuned in a systematic variation of the electric properties of the Schottky junctions. These results demonstrate the validity of using the ionic limit to model dipole engineering in oxides, and imply a larger freedom for structures in devices with ionic materials.

The 001-oriented SrRuO₃/Nb:SrTiO₃ junction was chosen as the model interface to tune the Schottky barrier height (SBH) using interface dipole control [3]. The interface dipole was fabricated by inserting LaTiO₃ or SrTiO₃ at the interface (Fig. 1a) and (b). In the resultant structures, SrO²⁻ is replaced by La⁺ in the case of LaTiO₃ insertion, and Ti⁷⁺ by Al³⁺ in the case of SrTiO₃ insertion. This ionic replacement creates an effect charge with the positive and negative sign, respectively, which are nominally denoted by (LaO⁺)⁺ or (AlO²⁻)⁻. This inserted charge induces a counter (screening) charge in the metal SrTiO₃ [Fig. 1(c) and (d)] to form an interface dipole. 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 using TiO₂-terminated 0.01 wt.% Nb:SrTiO₃ (001) substrates. After the LaTiO₃ or SrTiO₃ interlayer growth, 60 unit cells (uc) of SrTiO₃ were then deposited. The interlayer thickness was varied from 0 uc to 1 uc for LaTiO₃, and from 0 uc to 2 uc for SrTiO₃. The SBH was evaluated from electrical measurements as well as photoelectron spectroscopy.

As shown in Fig. 2(a), the current-voltage characteristics could be varied from Ohmic to rectifying (SBH = 1.7 eV), reflecting the SBH tuning by the interface dipole from the original SrRuO₃/Nb:SrTiO₃ junction with SBH = 1.3 eV. The sign of the interface dipole was consistent with the schematics shown in Fig. 1: the SBH was reduced by (LaO⁺)²⁺ and increased by (AlO²⁻)⁻. This systematic shift in the SBHs was also observed by photoelectron spectroscopy (Fig. 2(b)). The binding energy of Ti 2p₃/₂ core level was shifted to higher energy for the (LaO⁺)²⁺ insertion indicating the decrease in the SBH, and vice versa for the (AlO²⁻)⁻ insertion.

Thus, dipole engineering was demonstrated using SrRuO₃/Nb:SrTiO₃ Schottky junctions, taking advantage of the ionic character of these oxides. The SBH, originally 1.3 eV, was tuned using the interface dipole in a broad range from 0 eV to 1.7 eV. In a simple electrostatic picture, these interface dipoles can be understood to be formed by the inserted (LaO⁺)⁺ or (AlO²⁻)⁻ 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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