Probing the band alignment in rectifying $\text{SrIrO}_3/\text{Nb:SrTiO}_3$ heterostructures

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ABSTRACT

We have examined the band alignment in SrIrO₃/Nb:SrTiO₃ (001) heterojunctions at room temperature using three independent techniques: current–voltage and capacitance–voltage measurements and internal photoemission spectroscopy. We find near-ideal rectifying behavior across the junction, which provides the opportunity to establish the band alignment via Schottky barrier height extractions in the metal–semiconductor junction approximation. The Schottky barrier height deduced from these measurements agrees well with each other within ~14%, with an average value of 1.44 ± 0.11 eV. These results provide a foundation for designing oxide heterostructures to harness the strong spin-orbit coupling and electrochemical properties of strontium iridate.

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Oxide heterostructures incorporating strontium iridate have recently attracted much attention due to their versatile physical and chemical properties. For example, the large spin-orbit coupling that their 5d electrons host,^{1–4} together with the strong Dzyaloshinskii-Moriya interaction induced from artificially broken inversion symmetry, forms the basis for topological magnetotransport arising at SrIrO₃/SrRuO₃ heterointerfaces.^{5–7} Furthermore, an unexpectedly large charge transfer has also been reported in SrIrO₃/SrMnO₃ heterostructures, despite the nonpolar interfaces between them.^{8–10} In applications, embedding SrIrO₃ underneath an atomically thin shell in a core-shell heterostructure can be a promising candidate for further enhancing its activity and stability as an oxygen evolution reaction electrocatalyst.^{11,12} For all of these examples, the band alignment is one of the key elements that govern the electronic structure underlying these phenomena. For example, in the core-shell heterostructure, the position of the band edges of the capping (protecting) shell with respect to the SrIrO₃ core can fundamentally control the nature and degree of charge transfer. However, there has been relatively little work towards the experimental determination of the band alignment at heterointerfaces incorporating strontium iridate.

In this letter, we investigate the band alignment of rectifying SrIrO₃/Nb:SrTiO₃ (001) heterostructures at room temperature using current–voltage (*I*–*V*), capacitance–voltage (*C*–*V*), and internal photoemission (IPE) measurements (Fig. 1). Here, we use Nb:SrTiO₃ (001) as a reference substrate because the growth of the SrIrO₃ thin film is well-established on this substrate,^{1–5,13–16} and the band alignment of other complex oxides^{17–19} and elemental metals^{20–22} with Nb:SrTiO₃ has been widely studied. The heterostructures were grown using pulsed laser deposition. Nb:SrTiO₃ (001) substrates (0.01 wt. % Nb dopant concentration) were first annealed in 5×10^{-6} Torr O₂ at a substrate temperature of 940 °C in order to achieve a TiO₂-terminated surface with a perovskite step-and-terrace structure.²³ SrIrO₃ thin films were then grown in 50 mTorr O₂ at a substrate temperature of 600 °C. A 50 at. %-Ir-rich polycrystalline SrIrO₃ target was used in order to synthesize stoichiometric thin films considering the highly volatile dynamics of the ablated species, following previous studies.¹⁶ The target was ablated using a KrF excimer laser at a repetition rate of 5 Hz, incident at an angle of 45°. The heterostructures were then argon ion-milled into circular islands with a radius of 450 μm for the device isolation purposes and subsequently postannealed in oxygen at 200 °C

FIG. 1. (a) Schematic diagram of the measured SrIrO₃/Nb:SrTiO₃ (001) heterostructure devices. Au and In serve as ohmic contacts to SrIrO₃ and Nb:SrTiO₃, respectively. The device radius is 450 μ m. (b) Energy band diagram of the heterostructure based on the Schottky-Mott rule. E_C is the conduction band edge, E_F is the Fermi level, and E_V is the valence band edge. Within this framework, the Schottky barrier height ϕ is defined as the difference between the SrIrO₃ work function W and Nb:SrTiO₃ electron affinity χ .

for 1 hr to back-fill oxygen vacancies potentially generated during the etching process. Ohmic contact to SrIrO₃ was formed by e-beam deposition of Au using photolithography. The circular openings in Au contacts enable incident photons to reach SrIrO₃ without getting absorbed by Au during IPE measurements. Ohmic contact to Nb:SrTiO₃ was then formed by ultrasonic soldering of In. I - V measurements were performed in the DC mode using a semiconductor parameter analyzer. C - V measurements were performed using an inductance/capacitance/resistance (LCR) meter. For IPE measurements, light from a tungsten-halogen lamp was monochromatized by gratings and subsequently fed through an optical chopper and illuminated on the device. The photocurrent produced at the Schottky junction was measured in the AC mode using a lock-in amplifier synchronized to the optical chopper frequency. All measurements were performed at ambient conditions, with Nb:SrTiO₃ (001) serving as the ground.

We first characterized the crystalline quality of the as-grown thin film. Flat surface morphologies with a root mean square roughness of ~ 0.4 nm were observed, as measured by atomic force microscopy (AFM) shown in Fig. 2(a). A film thickness of 21 nm was determined from X-ray reflectivity (XRR) measurements [Fig. 2(b)] corresponding well to the intended thickness, where the data are accurately fit by the simulation assuming an average film roughness of ~ 0.7 nm, in reasonable correspondence with the roughness determined locally by AFM. Note that thickness fringes can be observed over ~ 4 orders of magnitude, indicating the coherent and uniform growth of SrIrO₃. We further confirm the single-crystalline growth of the SrIrO₃ thin film by X-ray diffraction (XRD) measurements in Fig. 2(c). Only the family of (00L) peaks of SrIrO₃ was found, with no other peaks observed above the noise level of the measurement. This indicates the high-quality epitaxial growth of (001)-oriented SrIrO₃ thin films with a c -axis lattice constant of 3.99 Å on Nb:SrTiO₃ (001).^{11,16}

The device displays a near-ideal rectifying behavior with negligible reverse-bias leakage (below 10^{-8} A/cm²) at low bias, as evident from I - V characteristics at room temperature in Fig. 3(a). As a result, the rectification ratio of the diode approaches $\sim 10^8$ within a bias range

FIG. 2. Structural characterization of SrIrO₃/Nb:SrTiO₃ (001) heterostructures. (a) AFM surface morphology of SrIrO₃ (scan area, 2.5 μ m $\times$ 2.5 μ m). (b) X-ray reflectivity measurements. The data (solid circles) are well fit by the simulation (solid line), which models 21 nm thick SrIrO₃ with an average roughness of ~ 0.7 nm. Thickness fringes over ~ 4 orders of magnitude are observed. (c) XRD patterns showing the family of (00L) SrIrO₃ film and Nb:SrTiO₃ substrate peaks.

of 1.5 V. This indicates that SrIrO₃/Nb:SrTiO₃ can be approximated well as a metal-semiconductor junction, which provides a useful basis to deduce the band alignment via Schottky barrier height (ϕ) measurements. Accordingly, we extract a barrier height ϕ_{IV} of 1.32 ± 0.01 eV from a fit to the exponential forward-bias regime via the thermionic emission model²⁴

$$\phi_{IV} = \frac{k_B T}{q} \ln \left(\frac{A^{**} T^2}{J_0} \right), \quad (1)$$

where J_0 is the saturation current density, A^{**} is the reduced effective Richardson constant, k_B is Boltzmann's constant, T is the operating temperature, and q is the elementary charge. Here, we use A^{**} of 1.562×10^2 A cm⁻² K⁻².¹⁷ We also extract an ideality factor η of 1.12 ± 0.01 .²⁴ η is 1 in the ideal limit and deviates toward a larger value as other contributors become dominant, such as tunneling. Here, we find that η is near ~ 1 , comparing favorably to prior measurements on SrRuO₃/Nb:SrTiO₃,¹⁷ which indicates that thermionic emission is the dominant transport mechanism across the junction and that the SrIrO₃/Nb:SrTiO₃ (001) interface is relatively electronically clean without dominant interface defects. This can also be inferred from the non-polar nature of the interface, which would otherwise be a dominant source for the formation of interface states.⁸ Note that we further fabricated a device with 53 nm SrIrO₃, which shows identical I - V characteristics with those for 21 nm SrIrO₃ except for the high-bias regime governed by the series resistance of SrIrO₃ [Fig. 3(a)]. Moreover, the deduced ϕ_{IV} of 1.33 ± 0.01 eV and η of 1.15 ± 0.01 for 53 nm SrIrO₃ are in good correspondence with those for 21 nm SrIrO₃. This indicates that the interface is relatively robust against surface degradation commonly observed in SrIrO₃ thin films.¹⁵

FIG. 3. Extraction of the Schottky barrier height ϕ for SrIrO₃/Nb:SrTiO₃ (001) heterostructures. (a) Current-voltage (I - V) and (b) capacitance-voltage (C - V) characteristics and (c) internal photoemission (IPE) spectroscopy. The solid circles are the data, and the solid lines are the best linear fits. The inset to (a) shows the same data on a linear scale, emphasizing the rectifying behavior of the junction. (d) ϕ extracted from independent measurements. The solid line indicates the Schottky-Mott limit, for χ of Nb:SrTiO₃ as 3.9 eV,³³ and W of SrIrO₃ as 5.1 eV.³⁴

Figure 3(b) shows C - V characteristics of the device with 21 nm SrIrO₃ plotted as C^{-2} vs V . The uncompensated donor concentration N_D is deduced from the slope of the plot to be $1.45 \times 10^{17} \text{ cm}^{-3}$, which is about one order of magnitude smaller than the nominal concentration of $3.3 \times 10^{18} \text{ cm}^{-3}$. Here, a dielectric permittivity ϵ of 300 was used for Nb:SrTiO₃.²⁵ Despite the reduction of N_D , the data show a linear relation over the entire voltage range of the measurement. This indicates that the Nb dopants are uniformly distributed in the substrate throughout the depletion region, and the reduction of N_D is consistent with previous reports for this low density regime.¹⁷ From the linear intercept, we also deduce the built-in potential ψ_{bi} of $1.45 \pm 0.03 \text{ V}$. For nondegenerate semiconductors, ϕ_{CV} can be extracted directly from ψ_{bi} by correcting for the energy difference ζ between the conduction band minimum E_C and the Fermi level E_F .²⁶ However, Nb:SrTiO₃ with 0.01 wt. % Nb dopant concentration is in the degenerate regime, as evident from the temperature-independent Hall coefficient and metallic resistivity down to low temperatures.^{17,27} Therefore, further correction is required depending on its density of states.^{28,29} As a simple bounding estimate, assuming a single parabolic band with an effective mass m^* of $1.3m_0$ and N_D that we deduced above, we find that the energy correction required here is negligibly small, $\sim 0.3 \text{ meV}$, and thus, ϕ_{CV} is $1.45 \pm 0.03 \text{ eV}$.¹⁷

We further perform IPE spectroscopy on the same device to extract ϕ_{IPE} in Fig. 3(c). IPE is a direct, robust method for determining ϕ , by measuring the photocurrent across the junction while

illuminating monochromatic light with variable energy. For incident photon energy $h\nu$ lower than ϕ , no photocurrent is detected as the photoexcited carriers cannot overcome the energy barrier. ϕ is therefore detected as the threshold $h\nu$ above which photocurrent is generated across the junction. Quantitatively, ϕ can be deduced from the following equation for the photocurrent per incident photon P based on Fowler's theory:³⁰

$$\sqrt{P} \propto h\nu - \phi_{IPE}. \quad (2)$$

One unique advantage of IPE is that it does not require an external bias, allowing us to probe the intrinsic response of the junction in equilibrium without inducing any complexities arising from external electric fields. We have focused our measurements at energies $h\nu$ below 3.2 eV, the bandgap of SrTiO₃,³¹ since photoexcited electron-hole pairs from interband excitations in Nb:SrTiO₃ will dominate the photoresponse above this limit. From the extrapolation of the linear dependence near the threshold regime of $\sqrt{P}$, we extract ϕ_{IPE} of $1.53 \pm 0.08 \text{ eV}$. Note that the linear region extends over a relatively wide energy range from 1.6 eV to 2 eV, indicating that the response of Nb:SrTiO₃ can be approximated well as a semiconductor with a single parabolic band as noted above. But the data deviate away from the linear dependence above 2 eV and even display nonmonotonic behavior. This could be due to increased nonparabolicity of the conduction band of Nb:SrTiO₃. Furthermore, the nonmonotonic behavior at higher energies can be attributed to the activation of optical transitions from deep O-2p states to Ir- t_{2g} states near the Fermi level.³² These photoexcited carriers are in turn filtered by the Schottky barrier, which results in a reduced IPE signal relative to the lower energy signal without any O-2p $\rightarrow$ Ir- t_{2g} interband transitions.

Taken together, the average ϕ of $1.44 \pm 0.11 \text{ eV}$ deduced from independent measures corresponds well to each other within $\sim 14\%$, and we further compare it with the Schottky-Mott rule [Fig. 3(d)].²⁴ Based on this model, ϕ of an ideal metal-semiconductor junction is defined as the difference between the metal work function W and semiconductor electron affinity χ . Nb:SrTiO₃ has χ of 3.9 eV,³³ determined using photoemission spectroscopy, and SrIrO₃ has W of 5.1 eV,³⁴ giving $\phi_{SM} = 1.2 \text{ eV}$. Considering the simplicity of the Schottky-Mott model, this is in reasonable agreement with the extracted values within 9% – 22%. Band alignments approximately following the Schottky-Mott rule have also been observed in other oxide heterostructures and in conventional ionic semiconductors. This shows the relative robustness of ionic materials against the formation of localized interface/surface states, which would otherwise pin the Fermi level and drive band alignments far from the Schottky-Mott limit.^{24,35–37} We note however that the deduced ϕ is slightly larger than this simple limit. One possible origin of this overestimation may be the change of the degree of p - d hybridization in SrIrO₃ due to electron accumulation within the Thomas-Fermi screening length, which locally increases its work function near the interface.³⁸ Another possibility is the continuity condition of O-2p states imposed at the interface due to the corner-sharing oxygen network,³⁹ thereby further modifying the band alignment beyond the simple Schottky-Mott limit.

This overestimation has also been observed in prior studies on SrRuO₃/Nb:SrTiO₃ junctions,¹⁷ where both ϕ_{CV} and ϕ_{IPE} were larger than the Schottky-Mott limit. ϕ_{IV} was however significantly lower than this limit, which can be attributed to nonidealities present at the heterointerface, including image-force lowering, tunneling, or spatial

barrier inhomogeneities.^{17,24,40} Another interesting observation is that this discrepancy between ϕ_{IV} and ϕ_{CV} or ϕ_{IPE} self-consistently scales with η . SrRuO₃/Nb:SrTiO₃ junctions with $\eta \sim 1.53$ had a discrepancy as high as $\sim 51\%$, but our device shows improved correspondence by four-fold with $\eta \sim 1.12$. However, the relative difference between ϕ_{CV} and ϕ_{IPE} is within $\sim 8\%$ for both cases, independent of η . This indicates that $C-V$ measurements and IPE spectroscopy are robust against nonidealities present at the heterointerface and thus likely provide a more accurate measure of the barrier height.

In summary, we have carefully studied the band alignment in SrIrO₃/Nb:SrTiO₃ (001) heterostructures using three independent characterization methods. We find that the junction behaves as a metal-semiconductor diode, with highly rectifying behavior and minimal reverse-bias leakage below 10^{-8} A/cm² at low bias. Furthermore, the rectification ratio reaches $\sim 10^8$ within a bias range of 1.5 V. The three measures of the Schottky barrier height ϕ agree well with each other within $\sim 14\%$, giving an average value of 1.44 ± 0.11 eV in reasonable correspondence with the Schottky-Mott rule within $\sim 16\%$. This study, together with previously established band alignments between other complex oxides and SrTiO₃,^{18,19} provides a quantitative basis for designing the band alignment of oxide heterostructures between SrIrO₃ and other complex oxides to optimize internal electric fields interacting with strong spin-orbit coupling and charge transfer in electrochemical processes.

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