

## Controlling photovoltage responses at SrRuO<sub>3</sub>/SrTiO<sub>3</sub> heterostructures

Strontium titanate (SrTiO<sub>3</sub>: STO) has been regarded as one of the key transition-metal oxides owing to its chemical stability, non-toxic nature, and exotic electron correlation effects. Furthermore, the perovskite structure of the STO crystal enables us to design a rich variety of layered metal oxide materials by the epitaxial growth of oxide films. Recently, the photoinduced response of STO has attracted broad interest owing to its wide range of applications including solar cells, photodiodes, photoelectrolysis, and photocatalysts. As a photovoltaic component, STO crystals have a major advantage of being transparent to visible light, enabling new uses and functionalities that are fundamentally impossible using silicon-based solar cells. Regarding the use of photoinduced phenomena in technology, the generation of the photovoltage is the most fundamental optical response, and therefore extensive studies have been carried out to clarify mechanisms in the surface photovoltage (SPV) effect. The SPV effect is induced by photoexcited carriers near a surface or an interface. Thus, the SPV effect is expected to be sensitive to surface/interface band bending (i.e., the surface/interface band alignment). However, effect of the surface/interface band alignment on the photovoltage responses, especially on technologically important oxide surfaces, has not been well studied. In this study [1], therefore, we study the band-alignment dependence of the SPV effect of STO by controlling the band alignment at the STO surface via the epitaxial

growth of a SrRuO<sub>3</sub> (SRO) thin film.

We demonstrate that the photovoltage response in STO can be enhanced by more than two orders of magnitude by the epitaxial growth of a two monolayer (ML) SRO thin film (0.8 nm). Furthermore, we show that the photoresponse phenomenon can be understood from the band alignment. Since the perovskite structure has a major advantage for the fabrication of layered structures, the approach to controlling space-charge layers by the growth of an overlayer described in this study is fundamentally applicable for a variety of oxide heterojunctions, and can therefore be used to control and design optoelectronic devices such as high-efficiency photoelectrochemical devices and solar cells.

All photoemission spectroscopy (PES) experiments were conducted at SPRING-8 BL07LSU, where synchrotron radiation (SR), the second-harmonic generation of a Ti:sapphire laser (3.05 eV), and a time-of-flight electron analyzer were synchronized. Thus, as shown in Fig. 1(a), the time-resolved measurements at a delay time ( $t$ ) were performed by the pump (laser)-probe (SR) method [2]. Using a soft X-ray as a probe light, surface-sensitive experiments were performed. A two-ML thin film of SRO was epitaxially grown on a 0.05 wt% Nb-doped STO(001) substrate (Fig. 1(b)) by pulsed laser deposition (PLD). The film thicknesses were controlled by monitoring the intensity oscillations of a reflection high-energy electron diffraction spot. The STO and SRO/STO samples were cleaned by

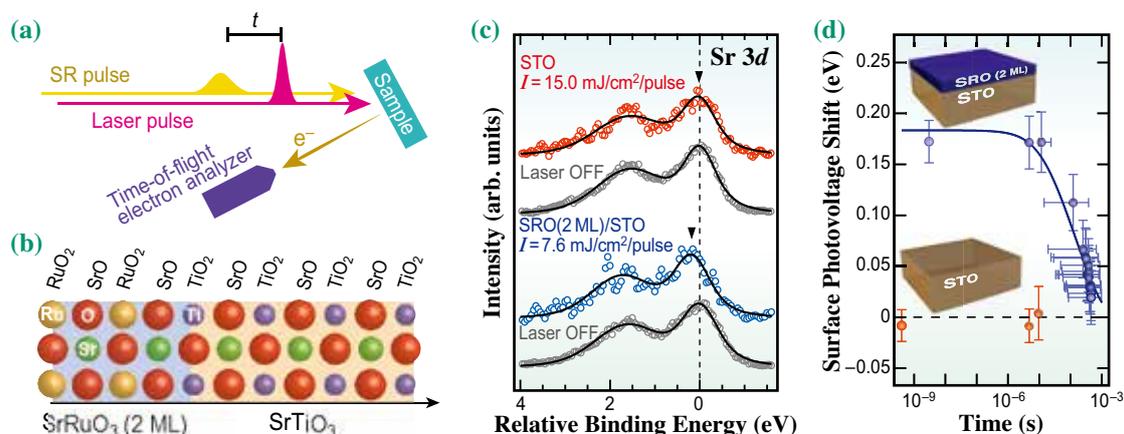


Fig. 1. (a) Schematic drawing of time-resolved PES measurements. (b) Schematic image of the atomic structure near the SRO(2 ML)/STO interface. (c) Energy shifts of Sr 3d peaks obtained at the STO surface and the SRO/STO interface, as monitored by time-resolved core-level spectra taken before and after pumping at a delay time of  $t = 9.6 \mu\text{s}$ . Here, pumping intensities of  $15.0 \text{ mJ/cm}^2/\text{pulse}$  and  $7.6 \text{ mJ/cm}^2/\text{pulse}$  were used for the STO surface and SRO/STO interface, respectively. The spectra are plotted with respect to the Sr  $3d_{5/2}$  peak before optical excitation (Laser OFF). The spectra were fitted by Voigt functions with backgrounds (solid lines) and the peak positions after the excitation are indicated by triangles. (d) Time dependence of the SPV shifts traced by time-resolved Sr 3d core-level PES measurements at STO (orange circles) and SRO/STO (blue circles). The solid curve shows the fitting result for the SRO/STO interface using the thermionic relaxation model [3].

annealing at 650°C under an oxygen pressure of  $1 \times 10^{-3}$  Pa for 60 min after introducing the samples into an ultrahigh vacuum (UHV) chamber.

Figure 1(c) shows Sr 3d PES spectra of the surfaces of STO and SRO/STO taken at  $t = 9.6 \mu\text{s}$ . Compared with the laser off position, the spectra show a clear shift of the peak position at the SRO/STO surface but not at the STO surface. This energy shift indicates the generation of SPV only at the SRO/STO surface. The relaxation of the SPV shifts is plotted in Fig. 1(d), where a relaxation time constant of 0.77 ms is obtained for the SRO/STO surface using a thermionic relaxation model [3].

Since the photoinduced phenomena result from the dynamics of the photoexcited carriers, which are governed by the electronic potential induced by the interface electronic structure, the drastic difference in the photoresponse between the SRO/STO interface and STO surface can originate from the band-bending structure near the surface/interface. Thus, in order to determine the band alignments, valence band (Fig. 2(a)) and Ti 2p (Fig. 2(b)) PES spectra were measured. The downward band-bending structure at the STO surface was determined from the energy position of the valence band maximum (VBM), indicating the formation of an accumulation layer at the STO surface as shown in Fig. 2(c). On the other hand, the upward band-bending structure at the SRO/STO interface was determined from the energy difference of the Ti 2p peak positions between the STO surface and SRO/STO interface, indicating the formation of Schottky barriers at the interface (Fig. 2(d)) owing to the formation of Schottky barriers. From the experimentally obtained conduction band minimum (CBM) positions, depth profiles of the carrier electron density in the STO substrates were simulated by self-consistently solving the Poisson-Schrödinger equations [4]. The calculated results reveal significant differences in the relaxation width of the band-bending structures. The potential variation on the bare STO surface indicates the strongly localized nature of the accumulated electrons near the surface (<3 nm). On the other hand, the depletion layer in the SRO/STO heterostructure was found to have a much longer relaxation length (>40 nm). The calculated results also show that the mean density of carrier electrons is about 200 times larger at the accumulation layer of the STO surface than at the depletion layer of the SRO/STO interface. The large mean density of the carrier electrons at the STO surface prevents the generation of SPV due to the pinning effect. Therefore, a higher laser intensity by more than two orders of magnitude is required for the STO surface to induce the same amount of the SPV shift as that induced for the SRO/STO interface when the number of photoexcited carriers is proportional to the laser intensity.

In summary, we have demonstrated that the interface electrostatic potential and the photovoltage responses in a metal oxide heterostructure can be controlled by atomic-scale design of the layered heterostructure. In the SRO/STO system, the character of the STO space-charge layer can be changed from an accumulation type to a depletion type by the growth of the SRO film. The resulting optical responses of STO are enhanced by more than two orders of magnitude.

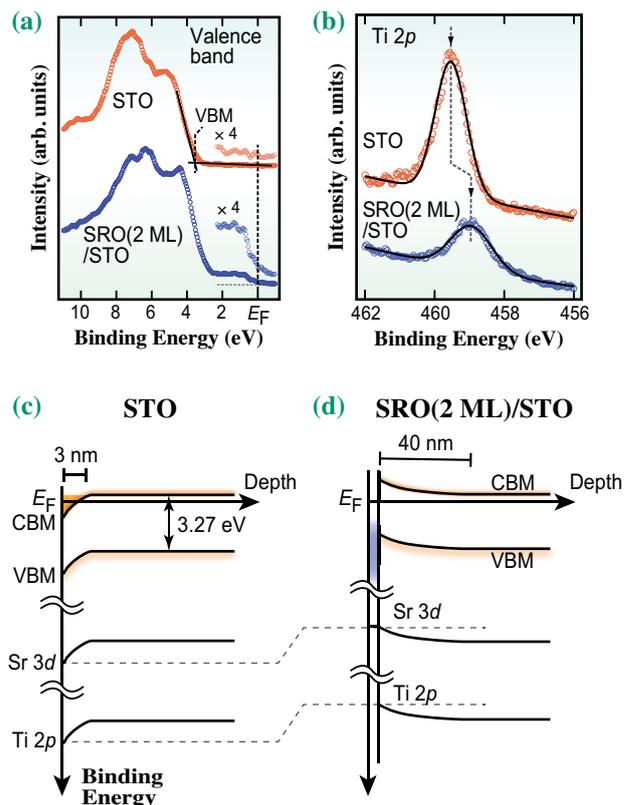


Fig. 2. (a, b) Valence band (a) and Ti 2p (b) photoelectron spectra of the STO surface and SRO(2 ML)/STO interface. (c, d) Band diagrams of the STO surface (c) and SRO(2 ML)/STO (d).

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