

Determination of the surface and interface phase shifts in metallic quantum well structures of perovskite oxides

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We propose an experimental approach to extract separately the surface and interface phase shift of standing waves in metallic quantum well (QW) structures composed of isostructural perovskite oxides. The “asymmetric” vacuum/SrVO₃/SrTiO₃ and “symmetric” SrTiO₃/SrVO₃/SrTiO₃ QW structures are fabricated in an epitaxial multilayer form. Using these metallic QW structures, the phase shifts at the surface (vacuum/SrVO₃) and interface (SrTiO₃/SrVO₃) are successfully obtained by analyzing a thickness series of angle-resolved photoemission spectra. The difference of the phase shift between the two boundaries reveals that nearly ideal quantum confinement is achieved at the interface, indicating that a SrTiO₃ layer acts as a useful potential barrier.

1 Introduction

Quantum well (QW) states have been a great contribution to the development of both fundamental physics and electric devices used for modern information technology [1-3]. Recently, metallic QW states were clearly observed for strongly correlated oxides by angle-resolved photoemission spectroscopy (ARPES): SrVO₃ (SVO) ultrathin films [4] as well as cleaved SrTiO₃ (STO) and KTaO₃ surfaces [5-7]. Such QW structures are relevant to understanding two-dimensional quantum confinement (phenomena) in strongly correlated oxides, which have attracted considerable attention for their potential use in the control of the novel functionalities of strongly correlated oxides using artificial structures.

In order to design the functionalities of the oxide QW structures, it is desirable to obtain knowledge of the complex interactions of the confined strongly correlated electrons at the boundaries, especially the phase shift

(reflection) of the electron at the surface and the interface. However, unfortunately, the phase shifts at the two boundaries cannot be extracted separately because one obtains the information as a “total phase shift” term of Φ , which is defined as the sum of the phase shifts at the surface ($\Phi_{surf.}$) and the interface ($\Phi_{interf.}$) in the quantization condition [1-3]. Therefore, the phase shifts at the two boundaries have been treated as the fitting parameters to describe the QW states, although the phase shift is an essential term to discuss the confinement condition in the metallic QW structures.

In order to overcome these difficulties, we propose a method of analysis to experimentally determine the phase shifts at the two boundaries using the “asymmetric and symmetric” QW structures, as shown in Fig. 1. These QW structures consist of isostructural perovskite oxides with a chemical formula of ABO₃. The symmetric A'B'O₃/ABO₃/A'B'O₃ QW structures, where electrons are geometrically confined inside the ABO₃/A'B'O₃ interfaces. Thus the total phase shift of this symmetric QW structure is twice the phase shift at the ABO₃/A'B'O₃ interface ($\Phi^{Sym.} = 2\Phi_{interf.}$). Meanwhile, the total phase shift of the asymmetric QW structure (vacuum/ABO₃/A'B'O₃) is obtained as the sum of the phase shifts at the ABO₃ surface and the ABO₃/A'B'O₃ interface ($\Phi^{Asym.} = \Phi_{surf.} + \Phi_{interf.}$). As a result, the phase shifts at the surface and the interface are separately determined by solving the simple simultaneous equations.

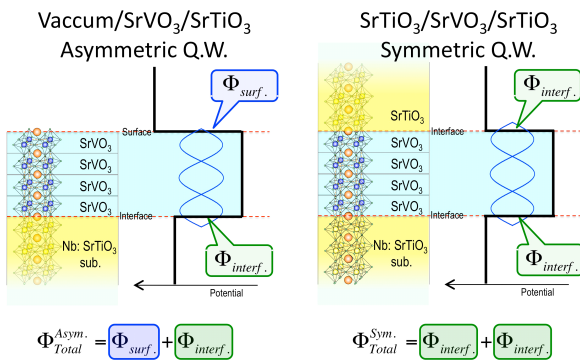


Fig. 1: Schematic illustration of the vacuum/SrVO₃/SrTiO₃ “asymmetric” and SrTiO₃/SrVO₃/SrTiO₃ “symmetric” QW structures.

2 Experiment

Digitally controlled SVO ultrathin films (asymmetric QW structures) were grown on atomically

flat TiO_2 -terminated Nbdoped STO substrates by a pulsed laser deposition method. For fabricating STO/SVO/STO (symmetric QW) structures, one monolayer of STO was subsequently deposited onto the SVO ultrathin films in the same growth conditions [8]. The thicknesses of SVO films and STO overlayers were controlled by monitoring the intensity oscillation of the reflection high-energy electron diffraction. The ARPES measurements were performed *in situ* at BL28A of Photon Factory, KEK. The energy resolution was set to 30 meV at a photon energy of 88 eV. All the ARPES measurements were performed at 20 K using linearly polarized light. The Fermi level (E_F) of the samples was referred to that of a gold foil.

3 Results and Discussion

Using the two kinds of metallic QW structures as shown in Fig. 1, we successfully determined the phase shift at the surface (vacuum/SVO) and the interface (STO/SVO) by analyzing an SVO-layer thickness series of ARPES spectra [8]. Figure 2 shows the structure plots obtained from the ARPES spectra of SVO films with and without an STO overlayer. For both of the QW structures, the quantized states look similar at the first glance. However, the quantized states located in the lower binding energy region exhibit differences in their peak positions between the two. Considering the structural difference in these QW structures, the differences in peak positions should reflect the degree of the quantum confinement at the surface and the interface, which is represented by the total phase shift in the phase shift quantization rule [1-3].

To estimate the total phase shifts for both of the QW structures, we simulated the structure plots by only changing the total phase shift, while other parameters were fixed [4,8]. These results are superimposed on solid lines in Figs. 2(a) and 2(b) for the symmetric and

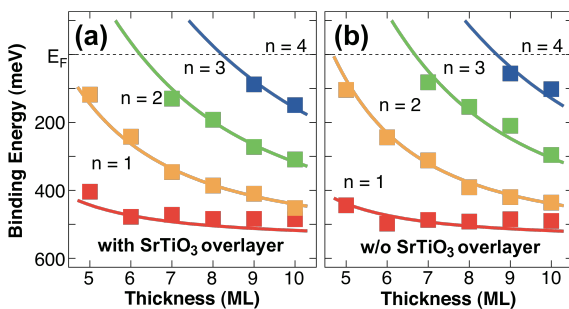


Fig. 2: Structure plot of SrVO_3 ultrathin films (a) with and (b) without a SrTiO_3 overlayer. The marker colors correspond to those of the triangles in Fig. 4. The markers and solid lines are the experimental data and simulated results based on the phase shift quantization rule, respectively.

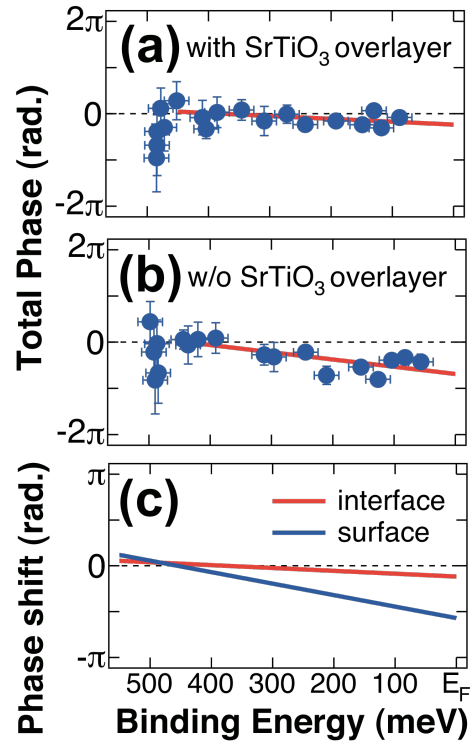


Fig. 3: Plots of the total phase shift of the metallic QW states in SrVO_3 layers (a) with and (b) without a SrTiO_3 overlayer as a function of binding energy. The markers with error bars denote the total phase shift obtained from analyzing the experimental data (see text for details). The solid lines are the results of the least squares linear fitting for the data. (c) The phase shift at the SrVO_3 surface and the $\text{SrTiO}_3/\text{SrVO}_3$ interface.

asymmetric QW structures, respectively. The simulated results reproduce the experimental results well, confirming that these observed states are derived from the quantized states in SVO layers in the metallic QW structures.

Figures 3(a) and 3(b) show the evaluated energy dependence of the total phase shifts in both QW structures. The experimentally obtained total phase shifts are well fitted by a least-square regression line as indicated by the solid lines in Figs. 3(a) and 3(b). The slopes of the total phase shifts as a function of binding energy are considerably different between the two QW structures. For an examination of the behavior of the standing waves at the boundaries of the SVO layers, we extracted the phase shifts at the surface and interface separately by solving the simple simultaneous equations (see Fig. 1). The separate phase shifts are shown in Fig. 3(c). As expected from the difference of total phase shifts in Figs. 3(a) and 3(b), the phase shift at the interface is almost independent of the binding energy and close to zero. On the contrary, the phase shift at the surface strongly depends on binding energy, and its absolute

value is considerably higher than that at the interface from 500 meV to E_F where the QW states were observed from the ARPES spectra. The phase shift at the surface is farther from zero than that at the interface, indicating that the standing waves are considerably better confined at the interface than at the surface. In particular, nearly perfect reflection of standing waves is achieved at the STO/SVO interface. This result suggests that the interfaces with STO are useful for the quantum confinement of the V 3d states in SVO.

Finally, we briefly discuss the reason why an STO layer acts as nearly ideal potential barriers in terms of the band diagram at the SVO/STO interface. The band diagrams drawn from the previous photoemission studies [4,9] are illustrated in Fig. 4. At the interface between the metallic SVO and the *n*-type semiconductor STO, a Schottky potential barrier of 0.9 eV is formed. Because STO has a wide band gap of 3.2 eV, the occupied V 3d states involved in the formation of the observed QW states in the energy range from E_F to 0.5 eV are located around the middle of the band gap of STO. Namely, the occupied QW states are energetically well isolated from the conduction band minimum (offset of ~ 0.9 eV) and valence band maximum (offset of ~ 1.8 eV) of STO at the interface. In such circumstances, it is difficult for an electron in the SVO layer to couple to any electronic states in STO.

Considering the band lineup at the SVO/STO interface in Fig. 4, the STO layers are regarded as a “vacuum” with higher permittivity for the V 3d electrons at a first approximation. STO is a quantum paraelectric material and its relative permittivity at the present measurement temperature of 20 K is more than 10,000 [10]. In such a high value of permittivity, the barrier-energy lowering near the interface due to the image force (image-force lowering known as the Schottky effect) [11] is negligibly weak, and the shape of energy potential near the interface approaches asymptotically to the intrinsic Schottky barrier. In other words, the abrupt potential well is formed at the interface, and consequently nearly ideal quantum confinement of V 3d electrons could be achieved. These results have an important implication for designing oxide QW structures; other oxide semiconductors with a wide band gap and a high permittivity are used as nearly ideal potential barriers to confine electrons in oxide heterostructures.

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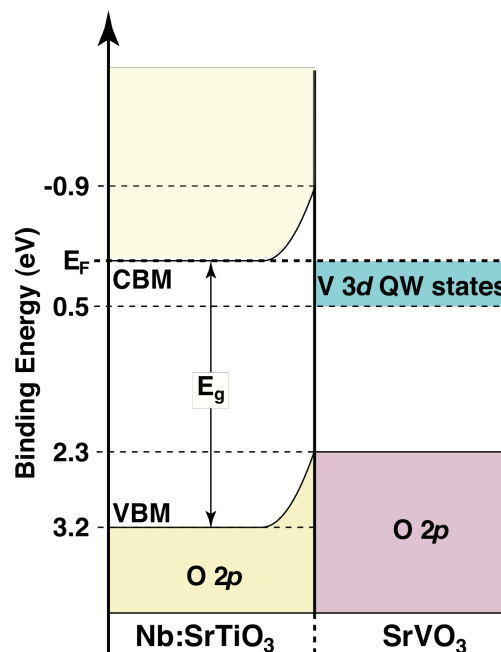


Fig. 4: Band diagram of the SrTiO₃/SrVO₃ interface deduced from the previous PES studies. CBM and VBM denote the conduction band minimum and valence band maximum, respectively. The V 3d conduction bands are energetically well isolated from both the CBM and VBM owing to the wide band gap of SrTiO₃ and its band lineup to SrVO₃.

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