論 文 の 内 容 の 要 旨

論文題目　Controlling the band alignments at complex oxide heterointerfaces
（複合酸化物界面におけるバンドアラインメント制御）

氏　　名　　立川　卓

I.　　　　Introduction

Transition metal oxides have attracted considerable attention owing to the wide variety of physical and chemical properties such as, transparent conductivity, catalytic activity, and multiferroicity [1, 2]. Many studies have focused on studying the heterointerfaces between these oxides with the aim of creating functional devices exploiting these unique properties. Given the central importance of carrier transfer across interfaces to the device functionalities, it is essential to establish a technique to control the interface energy band alignments for developing devices in general, as has been demonstrated in semiconductors and organic devices, but limited in oxide devices [3, 4]. The concept of band alignment control is based on the potential caused by an electrostatic dipole inserted at the interface. Due to the strong ionic bonding character of transition metal oxides, these materials can be viewed as alternate stacking of negatively and positively charged layers in a certain crystallographic orientation [5]. Despite its potential impact on designing wide range of oxide device structures, feasibility of this concept has been limited with two major challenges unanswered.

Firstly, the dipole tuning of band alignments has been demonstrated only at *iso-structural* epitaxial heterointerfaces between perovskites [5]. In order to generalize this technique, we aim to control the band alignments at a non-epitaxial interface between polycrystalline metal and binary oxides using perovskite dipole layers. The second challenge is to *increase* the band offset by forming stable dipoles at the interface. Currently, the tunable range of the band offset is -0.6 eV to +0.2 eV, with smaller range in increasing the dipole potential. If the band alignment can be both decreased and increased in a wide range, the materials selection for devices can be made on the intrinsic bulk properties and unconstrained by the band offset. In all of our studies, metal-semiconductor Schottky interface, where various measurement techniques are available, was selected as the model system and the effect of dipole layers were characterized by measuring the Schottky barrier heights.

For the first part, we focused on the Schottky junction between *polycrystalline* Pt and *single crystalline* anatase TiO_2. We used a perovskite insulator $LaAlO_3$, consisting of alternate stacking of LaO^+

and AlO^{2-} plane in the [001] orientation as the dipole layer with thickness less than 1 nm [5]. The good in-plane lattice match between LaAlO$_3$ and TiO$_2$ enables the formation of well-defined interface between the dipole layer and the TiO$_2$ thin films.

For the second part, previous study of bi-directional dipole tuning was based on using LaAlO$_3$ as the dipole layer on termination controlled SrTiO$_3$ (100) surfaces exploiting the iso-structural nature of the junction. Namely, for SrO terminated SrTiO$_3$ (100) surface, AlO$_2^-$ layer forms first and for TiO$_2$ terminated case, LaO$^+$ layer forms first thereby reversing the sign of the dipole. However, the obtained sign of the dipole was independent of the termination likely due to the instability of SrO-terminated SrTiO$_3$ (100) surface. Here, we used an alternative perovskite insulator AgTaO$_3$. Assuming the formal valence of Ag$^+$ and Ta^{5+} in AgTaO$_3$, negatively charged layer can be grown on a stable TiO$_2$-terminated SrTiO$_3$ (100) surface.

Experiment

We employed pulsed laser deposition for fabricating the oxide heterostructures. For the growth of LaAlO$_3$/TiO$_2$/LaAlO$_3$ (001) heterostructures, 0.3 at % Nb-doped TiO$_2$ (Nb:TiO$_2$) were grown at the laser fluence of 0.6 J/cm^2 and a repetition rate of 1 Hz under a substrate temperature (T_g) of 700 ^{o}C and oxygen partial pressure (P_{O2}) of 10^{-5} Torr. Single phase (001) oriented anatase TiO$_2$ film was confirmed by X-ray diffraction (XRD). The LaAlO$_3$ capping layer was grown by ablating a LaAlO$_3$ single crystal at a laser fluence of 0.5 J/cm^2 and the repetition rate was varied from 0.25 Hz to 3 Hz.

AgTaO$_3$ was grown on 0.02 at.% Nb-doped SrTiO$_3$ (100) (Nb:SrTiO$_3$) substrate which was annealed under 1000 ^{o}C and P_{O2} = 10^{-6} Torr to obtain TiO$_2$-terminated surface. Polycrystalline AgTaO$_3$ target was ablated at a laser fluence of 1.5 J/cm^2 and a repetition rate of 10 Hz under T_g = 700 ^{o}C and P_{O2} = 0.8 Torr.

II.   Results and discussions

1.   Pt/LaAlO$_3$/TiO$_2$/LaAlO$_3$ (001) Schottky junctions

There are two technical problems to stabilize the LaAlO$_3$/TiO$_2$ heterostructures. First is the degradation of the underlying TiO$_2$ layer depending on the LaAlO$_3$ top layer growth conditions [6]. We overcame this issue by the optimization of the repetition rate in LaAlO$_3$ growth. The second is the presence of (1 x 4) surface reconstruction of TiO$_2$ (001) after growth as shown in Figure 1 A that may prohibit the growth of epitaxial LaAlO$_3$ layer above it. In order to maintain (1 x 1) TiO$_2$ (001) surface, the as-grown anatase TiO$_2$ (001) surface was dosed with water and left in air for 2 hours prior to the LaAlO$_3$ deposition. No (1 x 4) RHEED pattern was observed below T_g = 625 ^{o}C in P_{O2} = 10^{-5} Torr for water treated TiO$_2$.

In order to observe the dipole effect induced by LaAlO$_3$ insertion, Pt/LaAlO$_3$/Nb:TiO$_2$ Schottky junctions with various LaAlO$_3$ thicknesses (0 – 2 u.c.) were fabricated. From current-voltage measurements, a clear rectification was confirmed. Capacitance voltage (C-V) measurements were performed to obtain the built-in potential (V_{bi}) as shown in Figure 1 B. V_{bi} linearly decreases with the thickness of LaAlO$_3$ confirming the active role of LaAlO$_3$ as the dipole layer. It should be noted that there
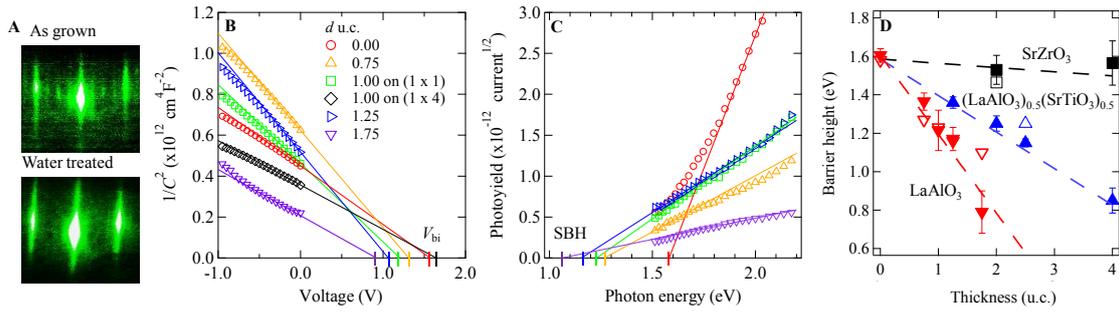
Figure 1. (A) RHEED pattern of as grown and water treated TiO_2/$LaAlO_3$ (001). (B) *C-V* data and (C) IPE spectra of Pt (5 nm)/$LaAlO_3$ (*d* u.c.)/TiO_2 (40 u.c.)/$LaAlO_3$ (001) at room temperature. Solid lines are linear extrapolation of *C-V* and IPE data. V_{bi} and SBH values obtained by these measurements are shown by solid lines crossing the horizontal axis. (D) Thickness dependence of of V_{bi} (filled) and SBH (open) for different dipole layers: $LaAlO_3$, $(LaAlO_3)_{0.5}(SrTiO_3)_{0.5}$, and $SrZrO_3$. Dashed lines are linear fittings of each data. Error bars of SBH are equal to the size of symbols.

is no V_{bi} shift in the case of 1 u.c. $LaAlO_3$ deposited on (1 x 4) reconstructed TiO_2 (001) surface indicating that unreconstructed anatase TiO_2 (001) surface is crucial in obtaining the dipole effect. Internal photoemission technique (IPE) was also utilized to obtain the SBH as shown in Figure 1 C. The square root of the photoyield (*Y*) was linearly fitted from 1.7 eV to 2.0 eV and extrapolated to the photon energy intercept to obtain the SBH. The SBHs monotonically shifted with increase in $LaAlO_3$ thickness. Values obtained from IPE and *C-V* are summarized in Figure 2 D. Except for the case of thick (1.75 u.c.) $LaAlO_3$, the V_{bi} and SBH showed excellent agreement.

In order to further confirm that the SBH change is attributed to the dipole effect, various perovskites having different average sheet charge densities were inserted to the Pt/Nb:TiO_2 interface. We utilized $SrZrO_3$ and $(LaAlO_3)_{0.5}(SrTiO_3)_{0.5}$ for interlayers which can be regarded as alternate stacking of $(SrO)^{+0}$/$(ZrO_2)^{+0}$ and $(La_{0.5}Sr_{0.5}O)^{+0.5}$/$(Al_{0.5}Ti_{0.5}O_2)^{-0.5}$, in the [001] orientation respectively. Since the dielectric constant of $SrZrO_3$ and $(LaAlO_3)_{0.5}(SrTiO_3)_{0.5}$ are approximately the same as $LaAlO_3$, their dipole moments are expected to be 0 and half of $LaAlO_3$, respectively. The SBH reduction induced by these interlayers is summarized in Figure 1 D. The gradient of the SBH reduction vs. $(LaAlO_3)_{0.5}(SrTiO_3)_{0.5}$ thickness is half of that of $LaAlO_3$. In the case of $SrZrO_3$, the SBH shows almost no change. These trends indicate that the SBH change is originating from the dipole moments formed by the ionic charges in the interlayer.

2.   Pt/$AgTaO_3$/Nb:$SrTiO_3$ Schottky junction

$AgTaO_3$ is a robust insulator among limited number of oxides with negatively charged A site layer. Major challenge in growing $AgTaO_3$ under UHV conditions lies in the large difference in the oxygen affinity between Ag and Ta. Thermodynamically, the decomposition temperature of Ag_2O is as low as 200 ^{o}C even under 1 atm oxygen, indicating that optimization of oxidization kinetics is crucial to obtain high quality $AgTaO_3$ films. Here we controlled the laser fluence and P_{O2} to provide sufficiently oxidizing
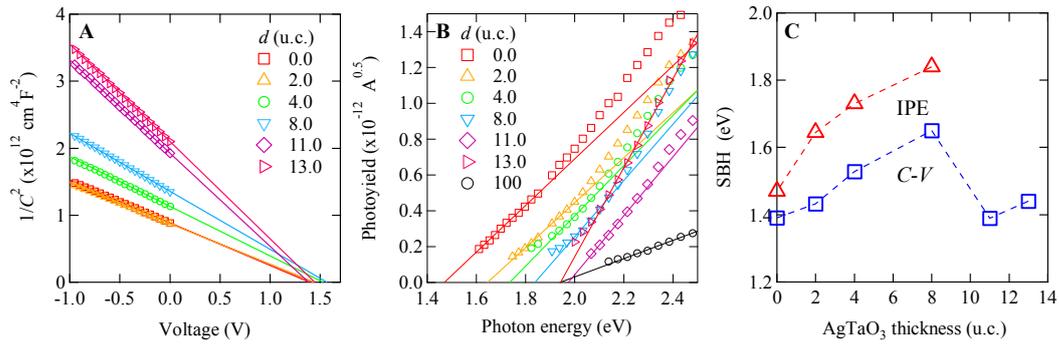
Figure 2. (A) *C-V* and (B) IPE data of Pt (5 nm)/AgTaO$_3$ (d u.c.)/Nb$_x$Sr$_{1-x}$TiO$_3$ (001) x = 0.002 at room temperature. Solid lines are linear extrapolation of *C-V* data and IPE spectra (C) AgTaO$_3$ thickness dependent V_{bi} and SBH. Dotted lines are guides for eye.

environment for the precursors, especially Ag, to react with oxygen. High quality AgTaO$_3$ film was confirmed by XRD 2θ scan and *c* axis lattice constant is 0.393 nm. AFM shows step and terrace structure up to the film thickness of 110 u.c.

Figure 2 shows the SBH characterizations of fabricated Pt (5 nm)/AgTaO$_3$ (0 – 14 u.c.)/Nb:SrTiO$_3$ (001). From the *C-V* measurements the V_{bi} potential monotonically increases with the thickness of AgTaO$_3$ up to 8 u.c. At thicknesses larger than 10 u.c., the V_{bi} abruptly drops to 1.35 eV identical to the value of direct Pt/Nb:SrTiO$_3$ junction. The SBH obtained by IPE shows exactly the same trend (Figure 2 B) up to 8 u.c. The SBH from the two measurements are summarized in Figure 2 C. The linear increase of barrier height indicates that the inserted AgTaO$_3$ layer clearly works as an electrostatic dipole. Assuming AgTaO$_3$ is purely ionic negative and positive charges stacking alternatively, the expected band offset change is 0.5 eV/u.c estimated by the directly measured dielectric constant of 88. The smaller band offset change is related to the covalency of bonding.

Conclusion

In this study, we aimed to expand the application of band alignment control by inserting interface dipoles at oxide interfaces which has been limited to all-perovskite interfaces. We successfully formed oxide dipole layers at polycrystalline metal and binary oxide interface and developed a technique to increase band offset by forming stable dipole which had been a challenge in previous studies. These results open the door to applying this band alignment tuning technique to various transition metal based devices.

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