Hysteretic current-voltage characteristics and resistance switching at an epitaxial oxide Schottky junction SrRuO$_3$/SrTi$_{0.99}$Nb$_{0.01}$O$_3$

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Transport properties have been studied for a perovskite heterojunction consisting of SrRuO$_3$ (SRO) film epitaxially grown on SrTi$_{0.99}$Nb$_{0.01}$O$_3$ (Nb:STO) substrate. The SRO/Nb:STO interface exhibits rectifying current-voltage (I-V) characteristics agreeing with those of a Schottky junction composed of a deep work-function metal (SRO) and an n-type semiconductor (Nb:STO). A hysteresis appears in the I-V characteristics, where high resistance and low resistance states are induced by reverse and forward bias stresses, respectively. The resistance switching is also triggered by applying short voltage pulses of 1 µs - 10 ms duration.

Recently, reversible resistance switching between two or multilevel resistance states has been found to take place by short voltage pulses at room temperature in capacitor-like devices composed of a wide variety of insulating perovskite oxides such as manganites, titanates, and zirconates sandwiched between two metallic electrodes. This resistance switching attracts considerable attention due to the potential for device application such as resistance random access memories (RRAM).

The origin of resistance switching, however, is still an open question. One of the possibilities is the bulk effect that a phase transition of perovskite takes place between insulating and conducting states, similar to the breakdown of charge-ordered insulating state in manganites induced by electric-field at low temperature.

The other is the interface effect, where voltage pulses reversibly alter the nature of potential barrier formed in the insulating (or semiconducting) perovskite in contact with metallic electrodes. We have recently shown that the resistance switching occurs at a Ti/Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ (PCMO) interface which exhibits Schottky-like current-voltage (I-V) characteristics, where Ti and PCMO can be regarded as a shallow work-function metal and a $p$-type semiconductor, respectively. A possible origin for the resistance switching is attributed to the change in Schottky barrier height (or width) by trapped charge carriers at the interface states. However, non-epitaxial structure and chemically incompatible materials combination make it difficult to characterize the transport properties and interface electronic structure in detail.

In the present study, we have investigated the transport properties of a heteroepitaxial perovskite oxide interface consisting of SrRuO$_3$ (SRO) deposited on (001) SrTi$_{0.99}$Nb$_{0.01}$O$_3$ (Nb:STO) single crystal substrate. The SRO/Nb:STO interface exhibits rectifying Schottky-like I-V characteristics with large hysteresis and the resistance can be changed by applying pulsed-voltage stress.

Epitaxial SRO thin films (100 nm) were grown on (001) Nb:STO single crystal substrates by a pulse laser deposition technique. Typical growth conditions were a substrate temperature of 700 °C and an oxygen pressure of 100 mTorr. After the deposition, the films were in-situ annealed at 400 °C for 30 minutes under an oxygen pressure of 500 Torr and then cooled down to room temperature. The crystal structure was analyzed by a four-circle x-ray diffractometer. The full-width at half maximum of the (002) rocking curve for SRO films is as narrow as 0.04 °. The in-plane lattice is compressively strained to match coherently with that of the substrate, resulting in a tetragonal lattice structure with an out-of-plane lattice constant of 0.395 nm.
The lower inset in Fig. 1 illustrates the sample structure and the measurement configuration. A gold electrode layer (230 nm) was deposited ex-situ on SRO by electron-beam evaporation. Mesas-structures with 100 μm × 100 μm in size were fabricated by conventional photolithography and Ar ion etching. The I-V characteristics were measured by the three-probe method using very large mesa (several mm²) as a quasi-ohmic voltage contact to Nb:STO. Positive bias is defined as the current flow from the Nb:STO to SRO. Typical I-V characteristics are shown in Fig. 1. The SRO/Nb:STO junction exhibits rectifying characteristics, which agree with the ones expected for a Schottky junction employing SRO and Nb:STO as a deep work-function metal and an n-type semiconductor, respectively. In the positive bias region, i.e., the reverse bias of the Schottky junction, the current scarcely flows at low bias and increases with increasing bias voltage above 2 V. Sweeping back to the negative voltage, i.e., the forward bias of the Schottky junction, the current suddenly increases at a certain voltage which corresponds to the flat-band condition or turn-on voltage. By reducing the temperature to T = 50 K, the turn-on voltage slightly increases, which agree with the temperature dependence of a typical Schottky junction.

The I-V characteristic at 300 K is plotted in a semilogarithmic current scale as solid lines in Fig. 2(a). There are large hysteresis in I-V characteristics at low bias voltage both in forward and reverse bias regions, which are not apparent in liner scale ones (Fig. 3). Here, we high resistance state (HRS) and low resistance state (LRS) for lower and upper branches of the hysteretic I-V characteristic, respectively. As can be seen, the forward bias scan to -1.4 V drives the junction to LRS and the reverse bias scan to 4 V turned the junction to HRS. LRS and HRS were kept unchanged when voltage polarity is changed through 0 V ((1) → (2) → (3) → (4)). The I-V curve at HRS in the forward bias region (4) is nearly a straight line, agreeing with a Schottky barrier model; forward bias current passing through a barrier with a height of φB is proportional to exp [−e(φB − |V|)/kB T], where e is electron charge and kB Boltzmann constant (see upper inset in Fig. 1). Although the junction gives rather leaky characteristics at low bias voltage both in forward and reverse bias regions, we discuss the hysteretic behavior and resistance switching hereafter with assuming that the SRO/Nb:STO junction is a Schottky junction. Therefore, the LRS can be regarded as possessing a reduced barrier height and/or an opened extra parallel current path such as tunneling.

Now, we examine the evolution of hysteresis by widening the span of the voltage scan. In Fig. 2(a), the bias voltage was swept as -1.4 V → 0 V → Vmax → 0 V → -1.4 V with Vmax varied as 1, 2, 3, and 4 V, where the junction was reset to LRS at the initial stage (see branches of (1) and (2)). When Vmax was 1 V, the LRS was hardly converted to HRS. As the Vmax was increased from 2 to 4 V, the junction was transformed gradually to HRS (see branches (3) and (4)) and the hysteresis was opened, resulting in the current differences over two orders of magnitude in low voltage regions. In Fig. 2(b), the bias voltage was swept as 4 V → 0 V → Vmin → 0 V → 4 V with Vmin varied as -0.8, -1.0, -1.2, and -1.4 V. In a similar manner to the cases of Fig. 2(a), initial HRS was gradually converted to LRS by increasing the voltage span in forward bias. Therefore, the barrier height reduction and/or an opening of additional current path can be developed by higher forward bias stress and they can be diminished by higher reverse bias stress.

When the junction was stressed by voltage pulses, the resistance was switched between rather steady HRS and variable LRS. The experiments were carried out as follows. First, the junction was brought into HRS by scanning the voltage to high enough reverse bias (Vmax = 4 V at 300 K and 50 K) as shown in Fig. 2(b). Then, voltage pulses of Vp = ±10 V were applied with a duration of τp. The resistance of the junction was evaluated by reading the current at a voltage bias (Vbias) of -0.5 V (300 K) or -0.7 V (50 K) as defined in Fig. 2(a). Extreme resistance values corresponding to the resistance with τp → ∞ were measured during I-V scans after the junction was biased to V = 4 V for HRS and to V = -1.4 V (300 K) or -1.6 V (50 K) for LRS. These values were defined as RH and RL as shown in Fig. 2(a) and plotted on the right ordinates in Figs. 2(b) and (c). When τp = 10 ms at 50 K, the resistance switching between HRS and LRS took place between almost RH and RL at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was decreased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was increased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was decreased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was increased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was decreased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was increased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was decreased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was increased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance. As τp was decreased, the resistance at LRS (RL) increased, while the resistance at HRS (RH) stayed constant close to RH at the first pulse and additional application of pulses scarcely induced further change of resistance.

So far, similar rectifying I-V characteristics have been seen in heteroepitaxial perovskite junctions composed of Sr(Ti,Nb)O3 and various metallic perovskites such as YBa2Cu3O7−x (Ba,K)BiO3 and (La,Sr)MnO3. In all cases, the rectification direction is consistent with that of a Schottky junction with regarding Sr(Ti,Nb)O3 and metallic perovskites as n-type semiconductor and deep work-function metals, respectively. The present SrRuO3/Sr(Ti,Nb)O3 junction is considered to be one of them. However, such distinct hysteretic behaviors as seen in Fig. 2(b) have never reported. Previously, we found that Ti/PCMO junctions showed rectifying I-V characteristics with just opposite combination of materials, namely shallow work-function metal and p-type semiconductor. The hysteretic direction and resistance switching between LRS and HRS are the same as the present case; reverse and forward biases turn the junction to HRS and LRS, respectively. Compared with Ag/PCMO or Ti/TiO2/PCMO interfaces, the present
interface is much better defined. The existence of resistance switching action should be related with some intrinsic mechanisms. We speculate the charging effect at the interface plays a role. By the voltage stresses in forward or reverse directions, the distribution of trapped charge would be altered, resulting in the modification of band lineup or tunneling probability. To explain retention or memory effects, one may have to take into account a self-trapping effect or configuration interaction, by which the trapped charge modifies a microscopic structure of bond arrangement or tunneling probability. To explain retention or memory effects, one may have to take into account a self-trapping effect or configuration interaction, by which the trapped charge modifies a microscopic structure of bond arrangement.

In summary, we have found that epitaxially and coherently grown heterojunction of SRO/Nb:STO shows rectifying \(I-V\) characteristics agreeing with that of a Schottky junction composed of a deep work-function metal and an \(n\)-type semiconductor. Well-developed hysteresis is formed so as to alter the junction resistance lower (higher) upon forward (reverse) bias stress. Presence of the resistance switching effect in heteroepitaxial structure should give a hint to elucidate the mechanism and also to enhancement of the device performance as memories in terms of atomic scale interface engineering.

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1. A. Odagawa for useful discussions.
2. Interface engineering.

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FIG. 1. Rectifying \(I-V\) characteristics of a SRO/Nb:STO junction measured at 300 K (a solid line) and 50 K (a dashed line). The upper panel of insets shows schematic electronic band diagrams of a Schottky junction, where \(\phi_B\) stands for barrier height. The left is under forward (negative) bias and the right is under reverse (positive) bias. The lower inset shows the sample structure and measurement configuration.

FIG. 2. (Color online) Hysteretic \(I-V\) characteristics of a SRO/Nb:STO junction measured with different spans of voltage scan. Bias voltage was swept as (a) \(-1.4 \text{ V} \rightarrow 0 \text{ V} \rightarrow V_{\text{max}} \rightarrow 0 \text{ V} \rightarrow -1.4 \text{ V}\) with \(V_{\text{max}}\) varied as 1, 2, 3, and 4 V, and (b) \(4 \text{ V} \rightarrow 0 \text{ V} \rightarrow V_{\text{min}} \rightarrow 0 \text{ V} \rightarrow 4 \text{ V}\) with \(V_{\text{min}}\) varied as \(-0.8\), \(-1.0\), \(-1.2\), and \(-1.4\) V. In both cases, chronological sequence of \(I-V\) curves is represented from (1) to (4).

FIG. 3. (a) Forward bias \(I-V\) characteristics of a SRO/Nb:STO junction measured at 300 K (solid line) and 50 K (dashed line). The filled and open symbols (stars and triangles) represent the high and low resistance states \((R_H^0\) and \(R_L^0\)), respectively. (b) and (c): Resistance switching behaviors at 50 K and 300 K, respectively. Pulsed voltage stresses of \(V_p = \pm 10 \text{ V}\) were applied to the junction reset to the high resistance state \((R_H^0)\) at the initial stage (before Time = 0), and the change of the resistance was recorded as a function of time for different pulse voltage durations \((\tau_p)\) of 1 \(\mu\)s, 100 \(\mu\)s and 10 ms. The resistance values are measured at \(V_{\text{bias}}\) as shown in (a).