Resistance dependence of photovoltaic effect in Au/SrTiO$_3$:Nb(0.5 wt %) Schottky junctions

D. S. Shang, J. R. Sun,[a)] L. Shi, Z. H. Wang, and B. G. Shen
Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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Photoresponse in the Au/SrTiO$_3$:0.5 wt % Nb Schottky junction with an electric field–tunable resistance between ~70 kΩ and ~900 MΩ has been experimentally studied. The most remarkable observation is the strong dependence of the open-circuit photovoltage on junction resistance and the invariance of the short-circuit photocurrent during resistance switching. These results, combined with a theoretical calculation based on the equivalent circuit model consisting of a diode in parallel with a resistor, suggest the occurrence of filamentary conductive channels across the interface of the junction under the impact of electric pulses, whereas the remaining Schottky barrier keeps completely unchanged. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3009285]

The phenomenon of electric field–induced reversible resistance switching between different states, called colossal electroresistance (CER) effects, has recently been observed in a large variety of materials.[1–9] The resistive transition finishes within tenths of nanoseconds, and the resultant resistance state can retain for days without considerable decay. The prompt response and the nonvolatile character manifest a potential application of this effect to the technology of random access memory. Despite the different models such as the carrier doping-induced Mott transition of the interfacial layer of the oxides,[10] an electrochemical migration of oxygen vacancies,[4,11] a charging effect of the Schottky-like interface,[5–7] and a random circuit breaker network model,[12] a widely accepted mechanism for this kind of CER effect is still lacking. According to the forms and locations of conductive paths, the CER effects can be classified into two types. One takes place at the interface due to the change in the contact resistance between metallic electrodes and insulating (or semiconducting) oxides under applied electric field, and the other occurs accompanying the formation and rupture of filamentary conductive channels in insulating oxides.[13] The former CER effect, which appears in most perovskite oxide-based devices, is particularly attractive because of its strong correlation with interfacial state. A typical example is the work done by Blom *et al.*[1] for the Schottky junction composed of ferroelectric oxides and metallic electrodes. The polarity alternation of the space charge in the ferroelectric layer in this diode leads to a variation in Schottky barrier, thus resistance. Field-induced alternation of interfacial barrier was also observed in the junctions without ferroelectric layer, such as the systems of M/SrTiO$_3$:Nb (M=Au, Pd, Pt, Ni, and La$_{0.7}$Sr$_{0.3}$MnO$_3$) and Ti/Pr$_{0.7}$Ca$_{0.3}$MnO$_3$.[5–7] However, there is also evidence that the Schottky barrier change is not necessary for the CER. For example, Fujii *et al.*[13] found no considerable capacitance changes, which couple directly to barrier width, accompanying the resistive transition in SrRuO$_3$/SrTiO$_3$:Nb. Similar phenomena were also observed in organic-based junctions.[14] It was proposed that the resistive transition originates from the change in conductance through additional tunneling paths rather than the change in barrier potential profile. These results actually imply different effects of electric pulses on Schottky barrier.

In addition to the current-voltage (*I*-*V*) and capacitance-voltage characteristics, many distinctive features can also be observed in a diode. Among them, photovoltaic effect is of special interest. It reflects the accumulation of nonequilibrium charge carriers, driven by the built-in electric field, on the two opposite sides of the junction and, therefore, can provide valuable information on interfacial potential.[15,16] As reported, the resistance change of the junction can be as large as 10 000-fold under the impact of electric pulses. It is therefore worthwhile to monitor the evolution of the photovoltaic effect as junction resistance varies. In order to clarify the effects of electric pulse on Schottky barrier, in this letter, we performed a comprehensive study on the photoresponse of the Au/SrTiO$_3$:0.5 wt % Nb Schottky junction that shows a field-tunable resistance between ~70 kΩ and ~900 MΩ.

The sample was fabricated by depositing, through a shadow mask, a Au electrode, ~20 nm in thickness and 0.4 mm in diameter on a 0.5 wt % Nb-doped SrTiO$_3$ substrate (STON) by magnetron sputtering under an Ar pressure of 5 Pa (base pressure ≈10^{-5} Pa). Two silver paint electrodes were prepared on the backside of the substrate. An appropriate electric pulse that can cause an electric breakdown was applied between the two Ag electrodes, and an Ohmic contact with the contact resistance of ~30 Ω was obtained. The current-voltage characteristics and resistance switching were measured by a Keithley 2601 SourceMeter. Bias voltage of 0.05 V was used for resistance measurement. The bias voltage directs from Au to STON is defined to be positive.

An excellent rectifying behavior well described by the Shockley equation and an obvious *I*-*V* hysteresis are observed, which reveal the Schottky-like character of the sample and the nonvolatile resistance changes for a *V* ascending-descending cycling (not shown). It should be noted that the *I*-*V* relations of Au/STON depend strongly on doping level and the electric hysteresis could be unobvious in the junctions with considerably lower Nb contents.[17] The presence of interfacial defects when the Nb content is high may favor an electric modification of the junction.

The junction oscillates between two states with, respectively, resistances of 40 kΩ and 900 MΩ as bias voltage of pulses alternates between 3 and 6 V (pulse width=1 ms). By

[a)]Author to whom correspondence should be addressed. Electronic mail: jrsun@g203.iphy.ac.cn.

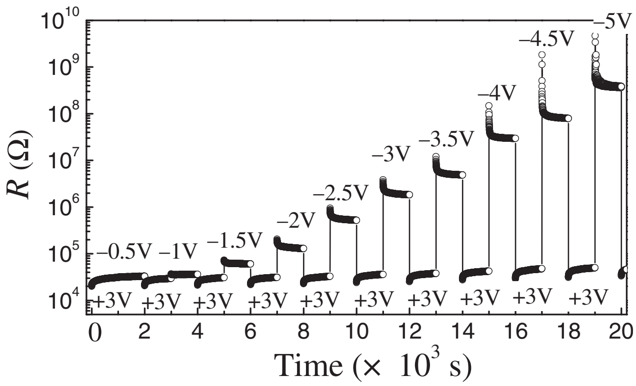

FIG. 1. Resistances of the Au/STON junction triggered by electric pulses with different polarities and amplitudes. Pulse width was fixed at 1 ms. Readout voltage is 0.05 V.

carefully adjusting the amplitude of reverse pulses, as shown in Fig. 1, a series intermediate resistance states can be obtained. The obtained resistance states are stable after an obvious relaxation, persisting for hours without considerable decaying.

It is obvious that the junction resistance has a close relation with Schottky barrier. This suggests the possibility of a concomitant change in photovoltaic effect with the resistive transition for any change in Schottky barrier; thus the build-in field will have a direct photoresponse. To get the information on interfacial state, photovoltage and photocurrent were further measured by exposing the sample with different resistances to an array of light emitting diodes (wavelength=460 nm), which gives rise to a uniform illumination. The light intensity, monitored by a photometer, was controlled by the bias voltage on the light emitting diode. All the measurements were conducted at room temperature. The experiment procedures are as follows: at first, the junction was triggered to a predetermined resistance state by appropriate electric pulses, and then, after the maintenance of 30 min for stabilization, the photovoltage and photocurrent were measured as functions of time.

Figures 2(a) and 2(b) present the open-circuit photovoltage (V_{noc}) and short-circuit photocurrent (I_L) of the Au/STON junction, obtained under a fixed light power of 0.4 μW. As expected, a voltage rise and a current flowing from STON to Au inside the junction are produced by light illumination. The most remarkable observation is the strong dependence of photovoltage on junction resistance (R_j). As shown in Fig. 3, V_{noc} exhibits a monotonic increase with R_j. The smallest and largest V_{noc} values detected are ~0.003 and ~57.6 mV, respectively, corresponding to the lowest ($R_j \approx 70$ kΩ) and highest ($R_j \approx 900$ MΩ) resistances. Different from photovoltage, however, I_L exhibits an invariant value of ~33.5 pA for a fixed light power of 0.4 μW, regardless of the change in junction resistance.

According to the semiconductor theory, there is a simple relation between photocurrent and interfacial barrier: $I_L \propto (L_p + L_n + W)G$, where L_p and L_n are diffusion lengths of holes and electrons, respectively, W is the barrier width, and G is the yield of photoexcited carriers.[16] If the resistance switching with the high-to-low ratio of $\sim 10^4$ originates from an alternation of the Schottky barrier, this change will be ~25%. It implies a reduction in the photocurrent from ~33.5 to ~26.0 pA while resistance drops as revealed by a

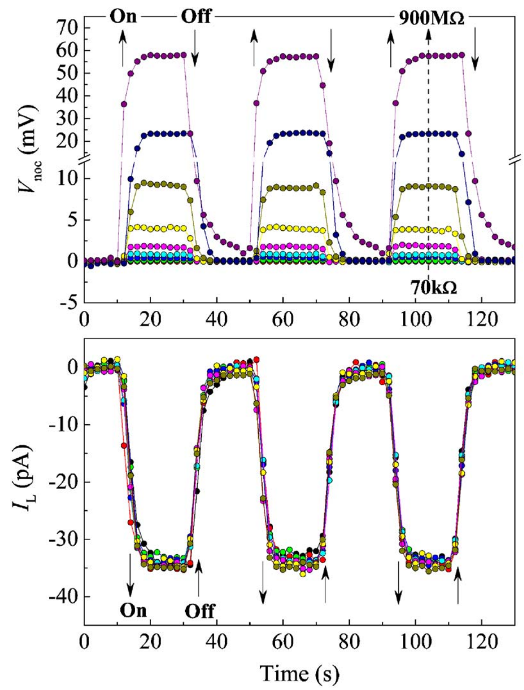

FIG. 2. (Color online) Photovoltage (a) and photocurrent (b) produced by light illumination for the Au/STON junction in different resistance states. The resistance ranged from 70 kΩ to 900 MΩ. Short arrows specify the time for the light on and light off.

rough estimation. This is a variation that can be captured by present experiments. Invariant I_L for different resistance states means the invariance of not only barrier height/width but also carrier diffusion lengths. However, the change in V_{noc} with junction resistance suggests the variation in the junctions. Considering the fact that the photovoltage is sensitive to the occurrence of conduction channels that short the interfacial barrier while photocurrent is not if the volume fraction of these channels is negligible compared with the junction region, existence of additional conductive filamentary channels across the Au-STON interface could be assumed to understand the apparently contradictory behaviors of V_{noc} and I_L. These channels strongly affect both the resis-

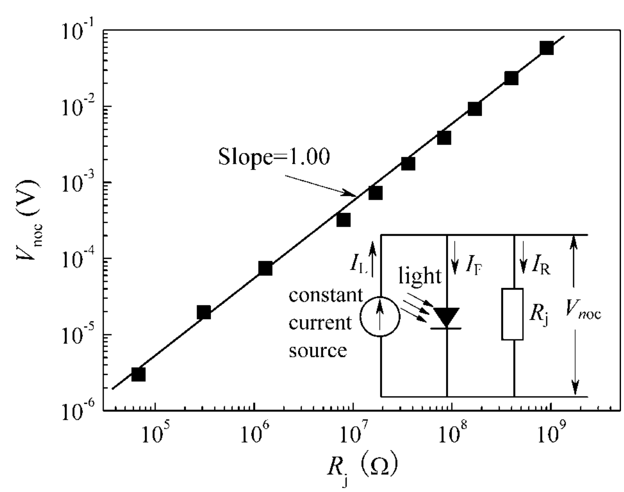

FIG. 3. Open-circuit photovoltages (V_{oc}) as functions of junction resistance. The slope of the fit line is 1.00, demonstrating the liner resistance dependence of V_{oc}. I_L=34 pA, directly calculated from the intercept of fit line with the V_{oc}-axis. Inset plot: the equivalent circuit consists of a diode in parallel with a resistor, modeling the photoelectronic processes in the junction.

tance, which is expected, and the photovoltage and the experiment results can be understood in this scenario as will be seen below.

On the basis of semiconductor theory, there is a one-to-one correspondence between I_L and true-open-circuit voltage (V_{oc}), $I_L=I_s[\exp(eV_{oc}/nk_BT)-1]$, where I_s is the saturation current and n the ideality factor of the junction.[16] From the I-V characteristics of the junction, $I_s \approx 5$ pA and $n \approx 3$ were derived. In fact, if photocurrent is unchanged, that is, the Schottky barrier (or I_s) is unchanged, V_{oc} could be obtained based on the above equation: $V_{oc} \approx 0.2$ V. In contrast, in the presence of filamentary conductive channels, the photocurrent can find its way from one pole of the junction to another, yielding a voltage drop of $V_{noc}=RI_R$ over the diode, where R is the resistance of conductive channels and I_R is the photocurrent in the existence of the load R. According to I_s value, the theoretical resistance of the Schottky diode is estimated to be ~ 24 GΩ, much larger than the resistance we measured. Thus, the measured junction resistance is mainly contributed by the conductive channels, namely, $R_j \approx R$. We simulate the photoelectronic processes in the junction in this case by an equivalent circuit consisting of a Schottky diode in parallel with a resistor (inset of Fig. 3). It is obvious that the current flowing through the parallel resistor is $I_R=I_L-I_F$, where $I_F=I_s \exp(eV_{noc}/nk_BT)$ is the forward current of the Schottky diode. These analyses lead to an explicit expression for V_{noc},

$$V_{noc} = R_j[I_L - I_s \exp(eV_{noc}/nk_BT)]. \quad (1)$$

A direct analysis shows that $I_F \ll I_L$ for the R_j range studied; this implies a simple linear relation

$$V_{noc} \approx R_j I_L. \quad (2)$$

As illustrated in Fig. 3, V_{noc} indeed shows a linear increase with R_j at a rate of $I_L \approx 34$ pA, which is a value consistent with the experimental data quite well [$\sim$33.5 pA in Fig. 2(b)]. This is an unambiguous proof for the successful capture of the main features of the junction by the equivalent circuit in Fig. 3.

Based on the analysis of photovoltage, electric pulses influence only conductive channels, whereas both the V_{oc} and I_L, thus the junction, keep essentially unchanged during the resistive transformation. The conductive channels will shunt the interfacial barrier and bear the main current through the junction. This may be why the remaining Schottky barrier in the Au/STON junction seems to be completely unaffected by electric pulses. However, if the interface is so homogeneous that the formation of conductive channels is difficult, a uniform change in interfacial barrier could occur, which explains the previous observations by various authors that both local and uniform changes in interface seem to be possible. The measured V_{noc} is not an open circuit signal at all but a measure of the voltage on conductive channels when photocurrent flows. Different from the case of V_{noc}, the influence of conductive channels on I_L is shunted by the ammeter, which has very small impedance. As for the conductive channels, it has been reported that the anionic/cationic vacancies (ions), which act as dopants, exhibit considerably high mobility near crystalline defects, and their rearrangements under external field are possible.[18] The reversible migration of these defects, under the impact of electric pulses, may cause local breakdown of the interfacial barrier, resulting in the formation of conducting filaments. It is obvious that further studies are still required to well understand the nature of the conductive channels across the Schottky barrier and evolution of these conducting filaments under electric pulses.

In summary, we presented a systematic study on the photovoltaic effect on the Schottky junction $Au/SrTiO_3$:0.5 wt % Nb. The most remarkable observation is the strong dependence of the open-circuit photovoltage on junction resistance and the invariance of the short-circuit photocurrent during resistance switching. The distinctive photovoltaic effects can be understood based on an equivalent circuit model consisting of a diode in parallel with a resistor. These results suggest the occurrence of filamentary conductive channels across the interfacial barrier during resistance switching and invariance of remaining Schottky barriers.

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