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Photoresponse of the Schottky junction $Au/SrTiO_3$:Nb in different resistive states

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A systematic study on photovoltaic effects has been performed for the Schottky junction $Au/SrTiO_3$:0.05 wt %Nb, the resistance of which can be tuned, by applied electric pulses, between ~1 and ~200 MΩ. It is found that, despite the great change in junction resistance, the photocurrent across the junction is constant when the power and wavelength of incident light are fixed. The corresponding Schottky barrier, deduced from the photoresponse data is ~1.5 eV, independent of junction resistance. This result suggests the invariance of the interfacial barrier during resistance switching and the occurrence of filamentary conduction channels. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2978240]

Electric-pulse-induced resistance switching in transition metal oxides has attracted intensive attention due to its potential application to high speed, long retention, and nonvolatile memory. This kind of remarkable behavior has been observed in a large variety of oxides such as NiO, TiO_2, Cu_xO, $SrTiO_{3-\delta}$, Cr-doped $SrTi(Zr)O_3$, and $Pr_{1-x}Ca_xMnO_3$.[1–7] One of the most important features in the systems that show the resistance switching is the presence of a Schottky barrier near the metal-oxide interface. Sometimes the electroresistance is ascribed to a field-induced variation in the interfacial barrier. For example, based on an analysis of the current-voltage (*I-V*) characteristics, Blom *et al.*[8] claimed that the polarity change in the ferroelectric oxide, from which a junction has been constructed, could cause a variation in the Schottky barrier, thus the resistance change in the corresponding junction. As an alternative, Sawa *et al.*[9] believed that the change in the Schottky barrier is due to a charge trapping or release of the defects in depletion layer. A recent report by Park *et al.*[10] seemed to confirm the modification of the interfacial barrier by applied field. The authors observed a capacitance variation in response to resistance switching in the $M/SrTiO_3$:Nb junctions (M =Au, Pd, Pt, and Ni). On the contrary, Fujii *et al.*[11] argued that the potential profile of the Schottky barrier is unchanged during resistance switching because of the absence of hysteretic capacitance-voltage (*C-V*) dependences, and it is the opening/closing of filamentary conduction channels across the junction that leads to the nonvolatile resistance change. Indeed, experiments done for a point contact system formed by a metallic tip and a $SrTiO_{3-\delta}$ single crystal demonstrated the oscillation of the interfacial state between a Schottky barrier and a metallic contact under the driving of the electric pulses with different polarity.[4]

It is obvious that the roles played by Schottky barrier are still not very clear at present. To get a comprehensive understanding of the resistance switching, determinative evidence on the behavior of interfacial barrier under external field is required. We noted that most of the previous investigations are based on the analyses of the *I-V* and *C-V* relations. As is well known, a distinctive property of the Schottky junction is photovoltaic effect: Driven by the built-in field, the nonequilibrium charge carriers accumulate in two opposite poles of the junction, giving rise to an electric output.[12] In contrast, filamentary channels, if they exist, have no contributions to photovoltaic effects. Therefore, the photoresponse is an effect that distinguishes the roles of Schottky barrier and conduction channels. Based on this consideration, in this letter we performed a systematic study on the photovoltaic effect of an $Au/SrTiO_3$:Nb Schottky junction that can be adjusted between different states with the resistances from ~1 to ~200 MΩ. It is found that, in spite of the great change in junction resistance, the photocurrent is constant when the power and wavelength of incident light are fixed. This actually implies the invariance of interfacial barrier during resistance switching.

The sample was fabricated by depositing, through a mask, an Au electrode ~450 nm in thickness and 0.4 mm in diameter on a (001)-orientated $SrTiO_3$ substrate doped by 0.05 wt % Nb (STON) by magnetron sputtering under Ar pressure of 5 Pa (base pressure $\approx 10^{-5}$ Pa) at room temperature. Two electrodes of silver paint were prepared on the backside of the substrate. Some appropriate electric pulses that can cause an electric breakdown were applied between the two Ag electrodes to obtain an Ohmic Ag-STON contact. *I-V* characteristics and resistance switching were measured by a Keithley SourceMeter 2601. The voltage bias that drives current flowing from Au to STON is defined as positive. All the measurements were performed at the ambient temperature.

Figure 1 shows the semilogarithmic plot of the *I-V* characteristics of the Au/STON junction for the voltage cycling of $0 \rightarrow +3 \rightarrow 0 \rightarrow -3 \rightarrow 0$ V (sweeping speed 10 mV/s). A strong rectifying behavior and an obvious *I-V* hysteresis are observed. The former is a typical feature of the Schottky junction, while the latter is a signature of nonvolatile resistance changes. The overlap of ten cycles of *I-V* curves shows a good reversibility of the resistance switching.

Based on the thermionic emission theory, forward current density varies following the relation:[12]

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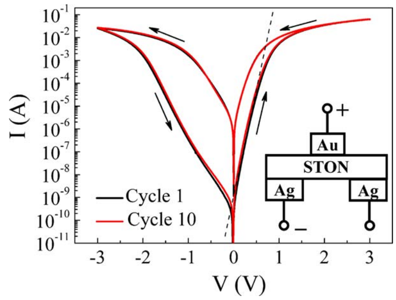

FIG. 1. (Color online) Semilogarithmic *I-V* characteristics of the Au/STON junction for the voltage cycling of $0 \rightarrow +3 \rightarrow 0 \rightarrow -3 \rightarrow 0$ V. Arrows indicate the sweeping direction. The inset plot is a schematic for the electrode setting of the sample. Dashed line is a guide for the eyes.

$$J_F = A^{**}T^2 \exp(-q\phi_B/k_BT)\exp(qV/nk_BT), \quad (1)$$

where A^{**} is the effective Richardson constant, ϕ_B is the Schottky barrier, q is the electron charge, n is the ideality factor, and k_B is the Boltzmann constant. The positive branch of the log *I-V* curve of Au/STON junction is well linear in the low bias region when the junction is in the high resistance state. A direct calculation based on Eq. (1) shows $q\phi_B \approx 0.88$ eV, deduced from the intercept of the linear log *I-V* curve with the current axis, where $A^{**} = 156$ A/cm^2 K^2 has been adopted.[13] The corresponding ideality factor is ~2, deviated significantly from the theoretical value 1. As reported, the work function of Au and the electron affinity of STON are ~5.2 eV (Ref. 12) and ~3.9 eV (Ref. 14), respectively. The anticipated Schottky barrier is therefore $5.2-3.9=1.3$ eV. The departure of n and ϕ_B from the expected values have been frequently observed in the Schottky junctions and could be a consequence of charge tunneling, spatial barrier inhomogeneities, or the presence of interfacial states.[11–13,15] The Schottky barrier of the low resistance state cannot be obtained based on Eq. (1) because of the significant log *I-V* nonlinearity in this case.

To get the information on resistance switching, a sequence of electric pulses with the amplitudes between −12 and +16 V and the width of 1 ms were applied to the Au/STON junction, and the resistance under the voltage bias of 0.1 V was recorded after each pulse as a function of time. As shown in Fig. 2, the junction resistance shows a high to low transition when stimulated by positive pulses whereas a reverse transition when the electric polarity is reversed. By carefully adjusting reverse pulses, different resistive states between ~1 and ~200 MΩ can be obtained. There is a simple relation between the amplitudes of electric pulses and the resultant resistance, the latter increases nearly exponentially with the former. The transition between different states is a transient process, as demonstrated by the appearance of significant overshooting followed by a slow relaxation of junction resistance.

As proved by a direct measurement, the resistance of STON is lower than 0.2 kΩ, and there is no *I-V* hysteresis. Therefore, the rectifying behavior (Fig. 1) and the high resistance value (Fig. 2) of the junction origin exclusively from the Schottky barrier, and it is the depression of this barrier or the formation of filamentary conduction paths that leads to the high to low resistance transition.

A distinctive feature of the Schottky junction is photovoltaic effect, which is a consequence of the migration of excited charge carriers in built-in electric field. As is well

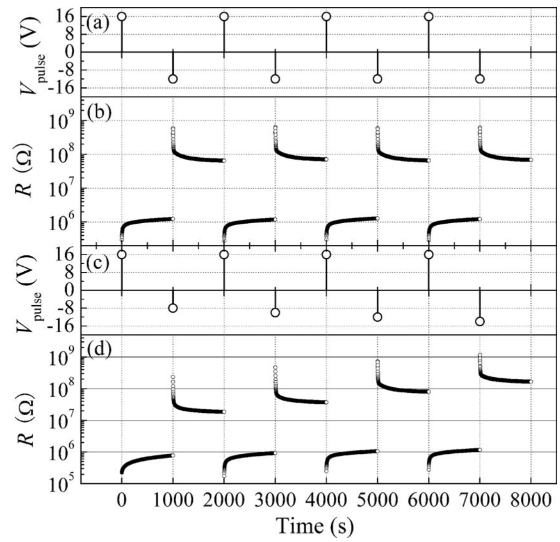

FIG. 2. Voltage pulses with the amplitudes of +16 and −12 V (a) and the corresponding resistance responses (b). Voltage pulses with amplitudes of +16, −8, −10, −12, and −14 V (c) and the corresponding resistance responses (d). Pulse width is fixed at 1 ms. Bias voltage is 0.1 V for resistance measurement.

known, electrons in metallic electrode can be excited by a light of the photon energy of hv (v is light frequency). When the condition $q\phi_B \leq hv \leq E_g$ is satisfied, the hot electrons can enter into the depletion region and then are attracted by the built-in electric field, yielding a photocurrent across the junction, where $E_g \approx 3.2$ eV is the band gap of $SrTiO_3$. It is obvious that any changes in Schottky barrier, thus the built-in field will have a direct response in photocurrent. On the contrary, filamentary conduction channels, if they exist, make no contributions to photovoltaic effect.

To reveal the influence of resistance switching on Schottky barrier, the photoresponse of the junction in different resistance states is further studied. The light sources are various dome light-emitting diodes (LEDs) with the wavelengths between 385 and 940 nm. The average light intensity was calibrated by a photometer and tuned by the voltage bias on the LED. By adjusting the amplitude of electric pulses, four different states with the resistances of ~2.5, ~24 MΩ, ~76, and ~200 MΩ, respectively, are obtained. To eliminate the effects of resistance relaxation, each resistance state is aged for 2 h before the photocurrent/photovoltage measurements. Figure 3 exemplifies the photocurrent as a function of time. It shows an instantaneous response of the junction to light illumination, as demonstrated by the switching of photocurrent between two definite values, respectively, corresponding to the "on" and "off" of the light source. The photoresponse is especially obvious to the light of 385 nm and weakens gradually with the increase in wavelength. The photocurrent varies from ~1.29 to ~0.04 nA corresponding to the wavelength/power from 385 nm/2.8 mW to 625 nm/0.6 mW. One of the most remarkable observations of the present work is the independence of the photocurrent of the junction resistance: Essentially the same photocurrent is obtained in different states if the wavelength and power of incident light are fixed.

According to Fowler, there is a simple relation between photoresponse (photocurrent per photon, R) and photon energy $R \propto (hv-\phi_B)^2$ when $hv-\phi_B > 3k_BT$.[12] Based on this equation the Schottky barrier can be experimentally deter-

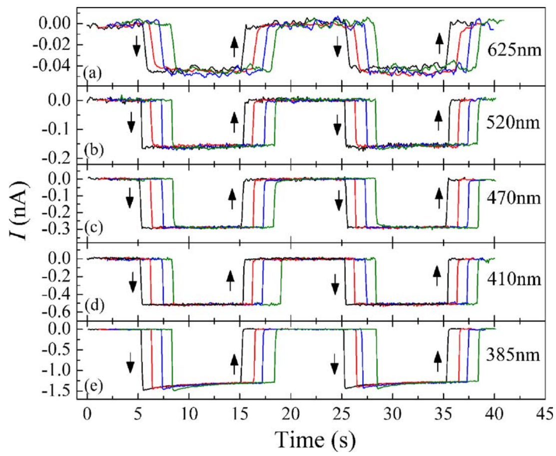

FIG. 3. (Color online) Response of photocurrent to light illumination. The black, red, blue, green line represent four different junction states with the resistances of ~2.5, ~24, ~76, and ~200 MΩ, respectively. Arrows indicate the variation of photocurrent when the light source is turned on and off (spot size ≈1 mm²).

mined. Figure 4 shows the square root of the photoresponse as a function of photon energy. An essentially linear $R^{1/2}$-$h\nu$ relation is obtained, which indicates the presence of a definite interfacial barrier. The barrier height is ~1.5 eV, which is simply the extrapolated value of the $R^{1/2}$-$h\nu$ curve in the energy axis. It is somewhat larger than that given by *I-V* characteristics while in fair agreement with the expected value from a simple analysis of the work functions of Au and $SrTiO_3$. As expected, a careful analysis indicates the absence of any detectable effects on energy barrier of the resistance changes. If resistance switching is due to the variation in ϕ_B, a direct calculation based on Eq. (1) shows $\Delta\phi_B \approx 0.12$ eV, corresponding to the resistance change from ~2.5 to ~200 MΩ. This is an alternation that can be captured by the present experiments.

To realize the resistive transition without changing the Schottky barrier, presence of tiny regions with a transport property sensitive to external field, called *active regions*, have to be assumed in the Au-NSTO interface. The active region works as a faucet, and electric pulses trigger the resistance switching by opening or closing the faucet.[16] That means the Au/NSTO junction behaves as a circuit consisting of a diode and a resistor connected in parallel, which mimics the Schottky barrier and the active region, respectively. The application of a positive voltage pulse depresses the value of the resistor but has little effect on the diode, causing the high to low resistive transition. The total area of the active region could be much smaller than that of the interface, which explains why the appearance of filamentary channels has no obvious effects on photoresponse. As for the role of the Schottky barrier, it provides a primarily high resistance state, which makes a colossal resistance drop possible during the resistance switching. In fact, a tunneling model where the resistance switching is due to changes in the carrier occupation of inhomogeneous regions of the interfaces was proposed be Rozenberg *et al.*[17] It demonstrated the possibility of local conduction via charge tunneling.

In the scenario of filamentary conduction, inhomogeneous conduction, an independence of resistance on electrode sizes of the order of the distance between filaments is expected. It is obvious that further studies are required to get a deep understanding of the nature of the active region and the effect of the Schottky barrier.

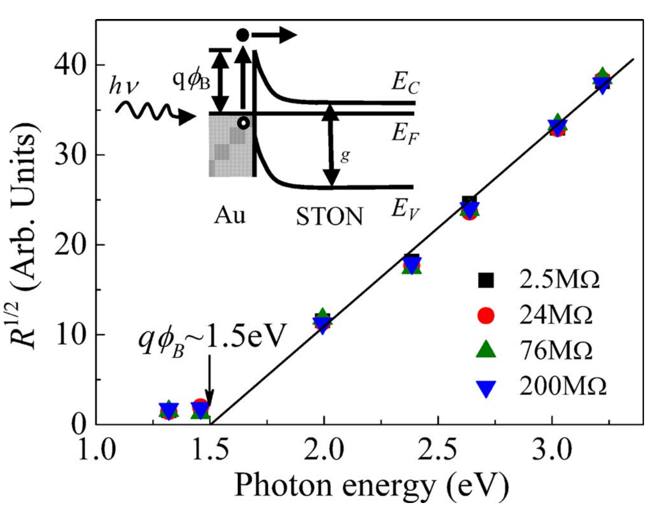

FIG. 4. (Color online) Relationship between the square root of the photoresponse and the photon energy in different junction resistance states. The straight line is a guide for the eyes.

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