Electric pulse induced resistance change effect in manganites due to polaron localization at the metal-oxide interfacial region

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Combining pulse-probe measurements as well as local transport measurements in an electron microscope system by a simultaneous monitoring of the structural changes, we show that the nonvolatilе electric pulse induced resistance change in Ca-doped praseodymium manganite is related to a polaron order-disorder transition, modified by electronic band bending in the vicinity of an interface to a metallic electrode. A pronounced resistance change requires a critical distance between the two electrode and/or oxide interfaces to form an insulating incommensurate polaron-ordered phase during the initialization of the device. Based on these observations, a qualitative model for the electronic structure of the metal-oxide interface is developed.

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I. INTRODUCTION

Materials which reveal a persistent resistance change after applying a short voltage pulse of a few hundred nanoseconds are of considerable interest for a new generation of fast and small power-consuming memory devices. This nonvolatile resistance change [electric pulse induced resistance (EPIR)] induced by voltage pulses of reversed polarity seems to be a rather common feature of oxides sandwiched by two metallic electrodes [e.g., ZrO2, Cr-doped SrTiO3, complex oxides such as Pr1−xCaxMnO3 (PCMO)]1. Therefore, several models have been applied to explain the effect as a Mott transition, the result of Schottky barriers, charge accumulation at the interface, and oxygen vacancy migration.

However, similarities in the transport behavior do not necessarily imply that the physical origin is the same, especially if highly correlated electron systems such as manganites are involved. These materials reveal a complex interplay of charge, orbital, and spin ordering, which give rise to several unusual effects such as electronic phase separation and colossal resistance effects induced by magnetic, electric, or photon fields (see Ref. 8 and references therein). In addition, these properties are strongly affected by sample preparation with respect to oxygen deficiency, residual strain, and quenched disorder.

Focusing on PCMO, the EPIR is neither a pure interfacial nor a pure volume effect. The choice of the electrode material seems to play an important role, and the major part of the resistance switching is located close to the interface in a region with thickness of the order of 100 nm. Nevertheless, a smaller but pronounced resistance change far away from the interface, away from the interface, and transport properties. These materials reveal a complex interplay of charge, orbital, and spin ordering, which give rise to several unusual effects such as electronic phase separation and colossal resistance effects induced by magnetic, electric, or photon fields (see Ref. 8 and references therein). In addition, these properties are strongly affected by sample preparation with respect to oxygen deficiency, residual strain, and quenched disorder.4

If the electrodes are separated by a macroscopic distance, the PCMO resistivity is controlled by the thermally activated hopping of small polarons with a Jahn–Teller activation energy in the range of 110–180 meV, depending on strain and disorder. The central ingredients of this quasiparticle formation are the electron-phonon coupling depending on the octahedral tilt. Strong or weak electron-phonon coupling gives rise to the limiting cases of a strongly located small polaron and a more bandlike large polaron. The scattering of those two types of quasiparticle will be quite different. In addition, small polarons are able to form a highly insulating type of charge and orbital ordered phase.

II. EXPERIMENT

In this Brief Report, we present direct evidence that electronic band bending coupled to electrically induced structural modifications of the MnO6 octahedra at the vicinity of an interface is a key ingredient for the remanent resistance changes. We systematically compare PCMO (x=0.33) sandwich structures, where electrode materials with different work functions were used [WPCMO=4.89 eV, WPt=5.65–6.35 eV, WAu=4.3–5.1 eV, WCr=4.44–4.65 eV, WCo=4.08–4.25 eV, and WRh=3.5–4 eV (from Ref. 19 and references therein)]. The deposition of PCMO thin films (dfilm=100–600 nm) was performed by pulsed-laser deposition (PLD) [Tdep=750 °C, P02=0.2 mbar (Ref. 20)] and by ion-beam sputtering (IBS) [Tdep=750 °C, P02=10−3 mbar]. Comparing both types of high-quality films on SrTiO3 by using structural and electrical characterization methods (such as x-ray diffraction, electron and atomic force microscopies, and transport properties), we find almost similar properties with respect to crystallographic quality, strain, ordered phases, resistivity, and colossal resistance effects. In particular, the length scale and temperature range of electronic phase separation between orbital and charge ordered and disordered phases for IBS films and PLD films are comparable.

The electrical properties of the devices were characterized by means of voltage-current curves and by low-current resistance, measured after the voltage pulse. The pulse width was between 150 μs and 4 ms. A first set of samples was prepared by a subsequent deposition at 750 °C of single-crystalline (100)-orientated Pt and (001)-orientated PCMO on (100) MgO substrates. To investigate the influence of the...
electrode material, small contacts (diameter of 500 μm) of different metals (Cu, Ag, Au, and Pt) and Sn-doped indium tin oxide (ITO) were deposited at room temperature on top of the PCMO layer. Each deposition step was performed by means of IBS, and the electrodes were jointed by bonding Al wires.

The influence of the PCMO layer thickness on the switching effect was analyzed in a second set of samples. SrTiO$_3$ substrates were coated at room temperature with a polycrystalline Pt template by IBS. In a preceding deposition step, PCMO was deposited by PLD, and Al wires were bonded directly on the PCMO surface as top electrodes (diameter of 70 μm). To study the local transport properties, a transmission-electron-microscopy (TEM)-ready bulk sample was mounted in a TEM setup including a scanning-tunneling-microscopy tip. Contacting the sample at a selected position, the Pt/Ir tip was used as a current source and the current-induced structural changes were monitored. These experimental techniques are described in more detail in Ref. 17.

III. RESULTS

Figure 1(a) reveals the three current-voltage curves of devices with single-crystalline Pt bottom electrodes and single-crystalline PCMO films of constant thickness (330 nm). If the top electrode is made from a noble metal (Au and Ag), the resistance is nonhysteretic and depends only marginally on the pulse voltage of up to 5 V. A remanent and pronounced switching is observed if ITO is used as a top electrode. Since the bottom electrode and the PCMO films are equivalent, this experiment clearly shows a strong influence of the electrode material. In contrast to an ITO oxide electrode, the switching voltage of noble metals seems to be much higher than 5 V and cannot be applied by long-term pulses because of the counteracting effect of the Joule heating. In addition, the joining technique has to be taken into account. If the top electrode is simply made by silver paste [inset of Fig. 1(a)], the sample reveals a remanent and pronounced switching effect, which is quite different from the almost Ohmic behavior of a sputtered Ag contact. We expect that this finding is related to an initialization process. The virgin resistance is much smaller than that in the low-resistance state and an electric stimulation is required to set the device in a switching state. In Fig. 1(b), the initial resistance of the devices is about 2Ω and increases to about 40Ω in the low-resistance state after a few pulses.

However, this initialization does not take place in the vicinity of the interface. We have prepared devices with equivalent bottom and top electrodes, for which only the PCMO layer thickness was varied [Fig. 1(c)]. All samples reveal a stable switching between a low-resistance and a high-resistance state by applying pulse of the same modulus but opposite sign. With the exception of the thinnest film ($d_{\text{film}}=100$ nm), the switching properties are almost unaffected by the thickness. It is out of the scope of this Brief Report to discuss the voltage amplitude dependence. We would only like to mention that an extraordinary high switching ratio is possible if the resistance is changed at one interface. Switching of both interfaces, e.g., that caused by a sufficiently high voltage, will cancel out the effect. We have indeed observed that the resistance of the high-Ohmic state increases with the voltage amplitude up to a maximum and rapidly drops down if the voltage is increased, e.g., from 2.7 to 3 V for the 300 nm thick sample.

Whereas the thinnest sample ($d=100$ nm) remains almost in a virgin resistance state with a small switching ratio having its maximum at 1.5 V [Fig. 1(c)], the same small voltage leads to an initialization if the thickness is 150 nm [Fig. 1(b)]. It is unlikely that such a small increase in thickness changes the interface properties to enable high-resistance states and pronounced switching. Therefore, our results imply a critical distance between the two electrodes (interfaces), which is required to fully evolve the effect. Most likely, this critical thickness is dependent on the deposition
from 0 to 16 μA and back to 0 μA [Fig. 2(d)], the superstructure gradually vanishes and reappears. First, the short modulation vector \( \sim 1.3b_0 \) disappears, while the long-range modulation of \( \sim 3.9b_0 \) remains up to 14 μA and renucleates first with decreasing current. During cycling current sweeps with successively increasing maximum current (8, 12, and 16 μA), the extension of the area with incommensurate ordering from the tip interface successively increases from an invisibly small state (virgin state) of over 40 and 50 nm to >90 nm.

### IV. DISCUSSION

A current-voltage dependence like the hysteretic one in Fig. 1(a) has been interpreted as a space-charge-limited current, which is accompanied by a hysteretic filling and depletion of traps.21 However, such similarity does not necessarily imply that electrons are involved in the switching effect instead of polarons, which control the bulk resistivity. Above the Ohmic range, the conductivity of hopping polarons increases exponentially with the voltage, but it has been pointed out by Stoneham et al.32 that the polaron mobility can be strongly modified in the vicinity of interfaces. Moreover, the presence of band bending can give rise to strongly modified \( U-I \) characteristics. Based on the charge density of the \( e_g \) conduction band of the order of \( 10^{17} \text{ cm}^{-3} \), band bending should be limited to screening lengths of a few unit cells (Fig. 3).

However, in contrast to a conventional Schottky contact, the spatial variation of the charge carrier density and the built-in electrostatic field due to band bending is coupled to the atomic structure of the oxide. Based on the doping dependent structural data of \( \text{Pr}_{0.75}\text{Ca}_{0.25}\text{MnO}_3 \),33 hole depletion \( x<0.33 \) significantly increases the local octahedral tilting and hole enrichment \( x>0.33 \) does not significantly change the octahedral tilting. Therefore, down-bending of the \( e_g \) conduction band strongly couples to the octahedral tilting and electric stimulation during the initialization process is able to move the zone of structural modification into the PCMO film [Fig. 3(b)].

Indeed, our local transport experiments in Fig. 2 prove that the change in polaron properties lies at the core of the resistance change. In Ref. 17, we have presented a detailed analysis of phase separation in bulk PCMO at room temperature. There, the \( 2b_0 \) commensurate superstructure modulation (space group \( P2_1nm \)) is due to a long-range ordering of the small Zener polarons. A sufficiently strong current induces a polaron melting transition (space group \( Pnma \)) and a persistent resistance decrease. The renucleation of the commensurate \( 2b_0 \) superstructure requires a current reversal.

In contrast to the bulk area, where in our samples only commensurate superstructure modulations with periodicities of \( 2b_0 \) and \( 3b_0 \) are observed, at the oxide-metal interface, an electrically induced formation and dissolution of incommensurate superstructure modulations are observed. The latter

[FIG. 2. (Color online) Observation of current-induced polaron order-disorder transition at the interface of PCMO and a Pt/Ir tip at room temperature in a transmission electron microscope. [(a)–(c)] High-resolution images showing the changes in the superlattice modulations along the crystallographic \( b \) direction at 0, 16, and 0 μA. The insets show the 2d Fourier transformations. (d) Line profiles of the Fourier spectrum of the lattice modulations along the \( b \) direction taken from the experiment. Three dashed lines between (000) and (020) show the incommensurable lattice modulations with the dominant Fourier amplitudes at \( b_x = 1.3b_0 \) and \( b_y = 3.9b_0 \).]
are actually present only near the interface after an electric stimulation. Its spatial extension is increased during the initialization process from the invisibly small state (virgin state) of the interface to an area of about 100 nm, in agreement with the critical thickness deduced from Fig. 1. Our model in Fig. 3 thus attributes the strong enhancement of the resistivity during the initialization process [Fig. 1(b)] to a spread of the high interfacial resistance area and its related structural changes due to polaron ordering into the PCMO film. During this process, the characteristic length scale of band bending is increased from a few nanometers to roughly 100 nm. Due to the higher interfacial resistance and larger local electric fields, this process is most likely induced at electrodes with down-bended band structure. After the formation of this remanent highly insulating state in a sufficient large area near one electrode during the initialization process, it can be switched by electric pulses of opposite polarity. An electric stimulated ordering and disordering of polarons depending on the polarity of the electric field was already observed in bulk PCMO, where a commensurate phase exists. At the interface, the direction of band bending and thus the formation and dissolution of incommensurate ordered phase directly depend on the sign of the applied electric field. There is no indication that the incommensurate lattice modulation is composed of nanodomains of different commensurate orderings. Therefore, a straightforward interpretation of this finding is that incommensurate polaron ordering directly reflects the band bending and related gradient in the polaron density toward the metal interface.

The qualitative model in Fig. 3 explains the occurrence of various \( U-I \) characteristics depending on the electrode materials and the preparation method [Fig. 1(a)]. A symmetric arrangement of noble metals such as Pt and Au gives rise to up-bending of the \( e_g \) conduction band on both oxide interfaces. The resulting electric behavior is then due to an in-series connection of the two Schottky contacts with opposite polarity. At low bias, this configuration generates an effective Ohmic behavior. Considering an ITO top electrode as an asymmetric configuration of the Schottky contacts with strong down-bending, the hysteretic \( I-V \) curve is related to the initialization of a switchable, polaron-ordered high-resistance state. In principle, small shifts of the ion positions in an electric field can significantly influence the electron-phonon coupling, i.e., the octahedral tilt and the Mn-O-Mn bonding angles depend on the electric field direction. This is directly evident from the noncentrosymmetric, polar structure of the \( 2h_0 \) ordering. In bulk PCMO, the pronounced twinning cancels out such effects over macroscopic distances. It is, therefore, worthwhile to mention that we indeed observed a current-induced detwinning, but we cannot completely exclude thermal assistance due to the Joule heating.

In summary, our results link the electric initialization of high-resistance states and the resistance switching effect in pulsed electric fields to the well-known bulk properties of polaronic hopping and its modification at the oxide-metal interfaces. The model of electronic band bending at interfaces with different work functions is well established in semiconductor physics. The suggested modifications for a system with strong electron lattice coupling and electric field induced structural changes qualitatively explain the strong resistance changes close to the interface and the moderate switching in the bulk, which is adapted from the same physical origin: a transition from small to large polarons related to the modification of octahedral tilting and change in resistance mechanism from trapping to scattering. In PCMO, the energy scale of the Jahn–Teller distortions (\( \sim 100 \) meV) is much smaller than the activation energy of oxygen vacancy migration (\( \sim 500 \) meV). However, the complete mechanism might be more complex, since oxygen vacancies and other interfacial effects such as misfit strain may influence the polaron properties and their resistance mechanisms. A general feature of oxides might be the coupling of band bending and strong local electric fields to the propagation of structural distortions such as oxygen vacancies or octahedral tilt. Oxygen vacancies are usually related to self-doping effects, where polaron hopping and localization must be considered as very common key transport mechanisms which can be modified at the vicinity of interfaces.

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