Interplay of cross-plane polaronic transport and resistive switching in Pt–Pr$_{0.67}$Ca$_{0.33}$MnO$_3$–Pt heterostructures

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Abstract. The identification of the cross-plane electric transport mechanisms in different resistance states of metal–oxide sandwich structures is essential for gaining insights into the mechanisms of resistive switching (RS). Here, we present a systematic study of cross-plane electric transport properties of Pr$_{0.67}$Ca$_{0.33}$MnO$_3$ (PCMO) thin films sandwiched by precious Pt metal electrodes. We observe three different transport regimes: ohmic, nonlinear and RS. The nonlinear regime is associated with colossal magneto-resistance (CMR) and colossal electro-resistance (CER) effects. In contrast to RS, the CMR and CER are volatile resistance effects which persist only during application of strong magnetic or electric fields and they are restricted to low temperatures. At low current densities, the device resistance is dominated by small polaron hopping transport of the PCMO film. At higher electric current densities near the switching threshold, the interface resistance starts to dominate and remarkably also exhibits thermally activated transport properties. Our studies also shed light onto the interplay of colossal resistance effects and RS: at low temperatures, RS can be only induced by reduction of the PCMO resistivity through CMR and CER. This clearly demonstrates the key role of the current density for controlling the amplitude of non-volatile resistive changes. Conversely, the CMR can be used as a probe for the switching induced changes in disorder and correlations. At small switching amplitudes, we observe slight changes in polaron activation.
energy which can be attributed to changes at the interface. If the switching amplitude exceeds 1000% and more, the CMR effect in the device can be reversibly changed. This indicates persistent changes in electronic or lattice structure of large regions within the PCMO film.

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1. Introduction

The electric resistance of transition metal–oxides can exhibit both volatile and persistent changes under external stimulation. In manganites, the reduction of the resistivity of bulk and thin film samples under application of magnetic and electric field by orders of magnitudes is associated to the colossal magneto-resistance (CMR), as well as the colossal electro-resistance (CER) effects. The CMR effect is attributed to a magnetic field induced phase transition from an insulating antiferromagnetic ordered phase found below the Neel temperature \( T_N \) to a ferromagnetic ‘metal like’ phase which is governed by magnetic double exchange [1]. CER effects are attributed to current driven polaron states and a resulting charge order (CO)–disorder transition [2, 3] below a critical CO temperature \( T_{CO} \) (≈ 230 K for \( \text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) (PCMO) with \( x = 0.3 \) [1]). Both colossal resistance (CR) effects are based on a subtle balance of different electronic correlations and can therefore be significantly affected by lattice disorder.

On the other hand, non-volatile resistive switching (RS) phenomena are observed in many metal–oxide–metal thin film heterostructures. Application of an external voltage of the order of a few volts between the facing top electrode (TE) and bottom electrode (BE) can change the initial virgin state (VS) resistance of the heterostructure to a high resistance state (HRS) or a low-resistance state (LRS). The induced resistance change is persistent, i.e. the HRS or LRS remains after removing the applied stimulation. By applying suitable, strong pulses one can ‘switch’ between these two stable states or even address intermediate resistance levels (multi-level), making these RS systems a promising candidate for resistive random access memory (R-RAM) applications [4]. In order to microscopically explain the non-volatile, rather temperature independent resistance switching, various models have been proposed, e.g. Mott transitions [5],

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Schottky barrier effects [6, 7], trapping controlled space charge limited currents [8] or electrochemical effects related to migration of oxygen/cation vacancies [9, 10]. Phenomenologically, the observed effects can be classified in unipolar or bipolar switching [11]. In the latter case, the resistance change can be only reversed by applying a voltage of opposite polarity. In addition, different types of switching topologies are observed, i.e. filamentary or interface type switching [12]. A universal microscopic switching mechanism independent of the selected material combinations, device geometries or the strength of the applied stimulus seems to be rather unlikely.

Hole doped manganite Pr$_{1-x}$Ca$_x$MnO$_3$ films which are sandwiched by precious Pt metal electrodes exhibit both, a non-volatile RS and the volatile CMR/CER effects. Since RS induces different resistance states, it must modify the underlying electric transport mechanism. Understanding the microscopic processes involved in RS thus requires understanding the electric transport mechanisms below and near the switching regime and how they differ in the VS, LRS and HRS states, respectively. The charge mobility in the hole-doped Pr$_{1-x}$Ca$_x$MnO$_3$ is controlled by the hopping of small hole polarons. Different transport regimes as a function of stimulation and temperatures have to be distinguished: for sufficiently small electric fields $E \leq E_c$, there exists an ‘ohmic regime’, where the electric resistivity is independent of $E$ and shows an exponential increase with decreasing temperature. At temperatures above half of the Debye temperature ($T_d/2 \approx 160$ K), the thermally activated motion of small polarons can be quite well described by the adiabatic Holstein model [13] and gives rise to a resistivity of the form

$$\rho(T) = \rho_0 T e^{E_A/k_B T},$$

where $\rho_0$ is a temperature independent pre-factor and $k_B$ the Boltzmann constant. In Pr$_{1-x}$Ca$_x$MnO$_3$ at doping level of $x = 0.33$ (in the following: PCMO), the activation energy $E_A$ is typically in the range of 130–150 meV. $E_A$ is reduced by magnetic fields ($\Delta E_A(B) \leq 25$ meV at $B = 9$ T) and increased by point like defects or octahedral disorder ($\Delta E_{\text{dis}} \leq 10$ meV) [14, 15].

For moderate electric fields and/or currents, small polarons exhibit a nonlinear electric transport regime, where the electric resistivity decreases with increasing field or current according to [16]

$$\rho_E(T, E) = \rho(T) \frac{E}{E_c(T) \sinh \left( \frac{E}{E_c(T)} \right)}, \quad E_c(T) = \frac{2k_BT}{ea}. \quad (2)$$

Here, $e$ is the electron charge and $a$ the polaron hopping length. The $\sinh^{-1}(x)$ term in equation (2) reflects the increase of rate of polaron forward over backwards jumps and holds as long as the processes remain adiabatic. It will break down for highly driven states of polarons, where the charge dynamics can partly decouple from the local lattice distortion [17]. In addition, strong thermal effects due to carrier transport induced phonon scattering and emission, similar to Joule heating set in. Such effects become relevant for the transport regime near the switching limit where the change of $T$ in equation (2) has to be taken into account. These changes can even result in a negative differential resistivity (NDR), which cannot be described by equation (2) alone (e.g. [18]).

In this contribution, we present a systematic study of the cross-plane electric transport properties of Pt–PCMO–Pt sandwich structures at varying electric field/current from the ohmic...
regime over the nonlinear behaviour (including CER and CMR) to the switching regime. We start with the analysis of PCMO film and interface contributions to the overall device resistance: the scaling of the device resistance with the geometrical sizes allows for a clear separation of current dependent bulk and interface resistances. The temperature and electric field dependence of the resistance confirm small polaron hopping as transport mechanism in this top-to-bottom geometry. Furthermore, the appearance of CMR and CER in this confined geometry with two close interfaces implies that the underlying electronic correlation effects are intact. The occurring CR effects are used in well-defined experiments to increase the current at low $T$ and, therefore, to enable remanent RS at various temperatures down to 10 K.

Finally, the change in CMR and polaron activation energies are used to analyse the changes of the polaronic transport system in different RS induced states (VS, LRS and HRS). Moreover, changes in transport properties of LRS and HRS formed in different switching regimes are examined, since in sufficiently large fields/currents a switching polarity reversal is observed [19] which points towards a second mechanism in this transport regime.

2. Experimental

The devices are based on a PCMO layer ($x = 0.33$) sandwiched by two Pt layers which serve as electrodes. The deposition of the layers was performed by ion-beam-sputtering (IBS) at a fixed Xe working gas pressure of $1.0 \times 10^{-4}$ mbar and $O_2$ partial pressure of $1.4 \times 10^{-4}$ mbar. First, as BEs, about 300 nm thick Pt films were deposited at 1023 K on (001) orientated single-crystalline MgO substrates, followed by 300 nm of PCMO, also at 1023 K. The selected oxygen partial pressure leads to nearly stoichiometric oxygen content as proven by the presence of a full CMR effect below $T = 110$ K which is suppressed otherwise. All samples under investigation reveal the orthorhombic crystal structure with dominating [001] orientation normal to the substrate, but with different degrees of twinning and different volume fractions ($<10\%$) of (112) misorientation.

The PCMO/Pt templates were spin-coated with photo resist (Allresist, AR-U 4040, thickness about 1.5 $\mu$m). Holes down to the PCMO top surface with a diameter of 2–7 $\mu$m are created in the resist by photo lithography techniques. These holes are finally filled with about 300 nm thick Pt layers, deposited at room temperature (RT) to avoid thermal decomposition of the resist. The resist remains on the sample, serving as an electrically insulating layer between the PCMO and the supply lines of the TE [20]. As an abbreviation, this type of device is named ‘pad devices’. A device cross-section scanning-electron-microscope (SEM) picture can be seen in figure 1(a).

Since small-sized TEs are faced by extended BEs in pad devices, we have also prepared devices with the same cross-section of both interfaces (‘pillar devices’) for well-defined overall current flow and improved symmetric interface resistance distribution. These devices were cut from a complete Pt/PCMO/Pt layer stack by means of focused ion beam (FIB). The TE and the PCMO film outside the pillar were removed down to the BE; the device cross-section is the same at both interfaces (see figure 1(b)). Using a micro manipulation system in an advanced SEM system, the TE was electrically contacted with a tungsten micro tip. This type of samples was used to measure the RT VS resistance for different PCMO layer thicknesses.

The electrical characterization was performed on various devices with different TE diameter prepared on the same template. The principle of the measurement is visualized in figure 1(c): in two-point geometry voltage or current pulses with duration of 2 ms are provided.
Figure 1. Device geometries and measurement configuration. (a) SEM cross-sectional view of a typical Pt/PCMO/Pt ‘pad device’. The size of the circular-shaped top-electrode is defined by the surrounding insulator (PMMA) deposited on top of the PCMO. (b) SEM picture of free standing ‘pillar device’. The layer stack of metallic TE (bright) on the PCMO film (dark) is cut down to the Pt BE (bright) by means of a FIB. The electric contact of the TE is realized with a micro manipulator tungsten tip inside a SEM. (c) Scheme of the ‘pad device’ with the applied voltage pulse sequence. (d) \( R_D \) (black symbols) and persistent \( R_{DP} \) (red symbols) resistances in dependence on the applied pulse voltage \( U_D \) (device details, see figure 5).

by a Keithley 2430 current source. The dependence of \( J–U \) characteristics on temperature \( T \) and applied magnetic field \( B \) was measured in a PPMS system (quantum design) at temperatures between 10 and 300 K in magnetic fields up to 9 T. The magnetic field was applied perpendicular to the substrate. The voltage \( U \) is defined with respect to the TE, i.e. a positive voltage pulse corresponds to an electron current from the bottom to the top. The current density \( J \) is calculated from the total current by using the TE area.

The current–voltage characteristic is either measured by setting the pulse voltage or the pulse current. Due to the presence of nonlinear branches with NDR and negative differential conductivity (NDC), only the combination of both measurement modes can give access to the...
full \( J-U \) characteristics. In experiments, where the thickness of the PCMO film \( d_{\text{PCMO}} \) has been varied, we can separate out the device resistance \( R_D \) (device voltage \( U_D \)), the bulk resistance \( R_B \) (voltage \( U_B \)) and interface resistance \( R_I \) (voltage \( U_I \)). In the voltage controlled mode, \( J-U \) is measured by voltage cycling \( U_D = 0 \text{ V} \rightarrow +U_{\text{max}} \rightarrow -U_{\text{max}} \rightarrow 0 \text{ V} \) with increasing \( U_{\text{max}} \).

In order to analyse the persistent response, a probe pulse of fixed voltage amplitude \( U_{\text{DP}} = 0.08 \text{ V} \) (close to the ohmic regime of the PCMO resistance) was applied after each excitation pulse \( U_D \). Figure 1(d) illustrates the dependence of the voltage dependent device resistance (black curve) \( R_D = U_D/I(U_D) \) and the corresponding persistent resistance (red curve) \( R_{\text{DP}} = U_{\text{DP}}/I(U_{\text{DP}}) \) which evolves due to the changes induced by the previously applied pulse voltage \( U_D \). Sufficiently high excitation pulses cause a crossover from the HRS to the LRS with a switching ratio \( \Delta R^+/R_{\text{LRS}} = (R_{\text{HRS}} - R_{\text{LRS}})/R_{\text{LRS}} \) which depends on \( U_{\text{max}} \). Here, \( R_{\text{HRS}} \) and \( R_{\text{LRS}} \) are the plateau values of the switching induced persistent resistance states. The crossover voltage \( U_c \) is defined by a \( 3\sigma \) criteria (the resistance change exceeds three times the noise level of the original resistance state). Similar definitions apply for \( R_D \), \( R_{\text{DP}} \) and \( J_c \) in the pulse current controlled measurement mode.

3. Results

3.1. Cross-plane film and interface resistances

In order to separate out the resistance contributions of the film and the metal–oxide interfaces, the device resistance \( R_D \) is systematically measured in FIB prepared ‘pillar devices’ as a function of PCMO thickness \( d_{\text{PCMO}} \), pillar cross-sectional area \( A \) and current density \( J \). In figure 2(a), \( R_D \) is normalized by the corresponding contact area \( A \) (\( R_D \times A \)) for several devices with a Pt TE deposited at 473 K. This normalized resistance \( R_D \times A \) is independent of the actual contact area \( A \) and only depends on the PCMO layer thickness \( d_{\text{PCMO}} \). This result also underlines a good sample quality/reproducibility of the device preparation and allows averaging values over several devices with the same \( d_{\text{PCMO}} \) (dotted lines in figure 2(a)).

In figure 2(b), these averaged specific resistances \( R_D \times A \) are plotted over the PCMO layer thickness and exhibit a linear dependence with a slope which depends on the applied current density. The linear dependence now allows for separating the overall resistance of the device in interfacial and bulk-like contributions. The cross-plane device resistance \( R_D \) can be described as a serial circuit of an interface and a bulk contribution, i.e.

\[
R_D = R_I + R_B = \frac{\delta_I}{A} + \rho_B \frac{d_{\text{PCMO}}}{A},
\]

where \( \delta_I \) is the combined contact resistance of both interfaces and \( \rho_B \) is the bulk resistivity of PCMO. Figures 2(a) and (b) imply that \( \delta_I \) and \( \rho_B \) are spatially homogeneous. For current densities of \( 1.0 \times 10^8 \text{ A m}^{-2} \) (ohmic regime), the slope corresponds to a resistivity of \( \rho_B = 1.1(5) \times 10^{-3} \Omega \text{ m} \). This nicely agrees with the typical ohmic bulk resistivity of about \( 10^{-2} \Omega \text{ m} \) in epitaxial thin films obtained in lateral geometry [21]. The interfacial contribution calculated from the extrapolation of the linear fit to zero thickness amounts to \( \delta_I = 194(9) \times 10^{-12} \Omega \text{ m}^2 \) for Pt top layer deposited at 473 K. These results for ‘pillar devices’ should be also valid for the ‘pad devices’ used in other experiments. Using the same type of PCMO/Pt layer stack and Pt TEs deposited at RT, the overall resistivity \( \rho_D = R_D \times A/d_{\text{PCMO}} \) of ‘pad devices’ amounts to about \( 1.5 \times 10^{-3} \Omega \text{ m} \) which is close to overall resistance value of about \( 1.8 \times 10^{-3} \Omega \text{ m} \) in pillar-like devices.

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Figure 2. Separation of bulk and interface resistances in Pt/PCMO/Pt pillar devices at $T = 300$ K. Pt top layers were deposited at 473 K. (a) Two-point resistance of several devices normalized by the electrode contact area $A$ is shown for various PCMO film thicknesses ($d_{\text{PCMO}}$) and measured at a fixed current density of $J = 1.0 \times 10^8$ A m$^{-2}$ (ohmic regime). Each point represents a single device. The dotted lines represent the averaged values for each $d_{\text{PCMO}}$ and the given $J$. (b) Linear dependence of the averaged $R_D \times A$ values on $d_{\text{PCMO}}$ for different current densities $J$ for the devices with 2 µm diameter. (c) Voltage and normalized resistance in dependence on current density. The bulk (red, solid), the interface (green, solid) contribution and the total device (black, solid) contribution are calculated from (b) for an exemplary PCMO thickness of 300 nm at 300 K. Both, the interface and bulk contributions can be fitted by equation (2) (magenta) in a $J-U$ range below the onset of the NDR of the bulk contribution (see text). For comparison, the experimental device values of a pillar device with 2 µm diameter and 300 nm PCMO thickness are also shown (black, open symbols).

The linear dependence of the device resistance on $d_{\text{PCMO}}$ and therefore the serial circuit model also holds for higher current densities in the nonlinear regime (figure 2(b)). However, slope and axis intercept decreases with increasing current density, since the actual measured resistance is reduced with increasing current density/voltage (see $R_D$ ($U_D$) in figure 1(d)). Therefore, we have used the linear dependence of $R_D$ on $d_{\text{PCMO}}$ to calculate the voltage/resistance contributions of the film and the two combined interfaces in dependence of
the current-density passing through the device at $T = 300$ K (figure 2(c)) for Pt deposited at 473 K. The calculations are exemplarily done for a pillar sample with $d_{\text{PCMO}} = 300$ nm.

For small current densities $J \leq 10^8$ A m$^{-2}$ (ohmic regime) we observe a resistance ratio of interface to bulk contribution $Q = R_I/R_B = 0.61(3)$. With increasing current density, $Q$ approaches one. Above a current density of about $1.1 \times 10^9$ A m$^{-2}$ the interface resistance dominates the overall device resistance ($Q > 1$). At the onset of persistent RS ($J \approx 6 \times 10^9$ A m$^{-2}$, $U_D \approx 0.55$ V), $Q$ is of the order of 3. This crossover between bulk dominated and interface dominated device resistance is accompanied by the appearance of a negative differential resistance (NDR: $dU/dJ < 0$) of the bulk contribution. For sufficient small current/voltages, the individual contributions in figure 2(c) can be fitted by using a current voltage dependence based on equation (2). For the bulk contribution we obtain $\rho(T)/E_C = 3.92 \times 10^{-9}$ m$^2$ A$^{-1}$ and $E_C = 2.8 \times 10^5$ V m$^{-1}$ ($d_{\text{PCMO}} = 300$ nm). For the interfacial contribution we obtain $\rho(T)/E_C = 1.35 \times 10^{-9}$ m$^2$ A$^{-1}$ and $d_I \times E_C = 0.14$ V where the thickness of the interface layer $d_I$ is unknown. Figure 2(c) implies that $E/E_C$ is larger in the bulk than in the interface area. Comparing the validity range of both fits, the bulk contribution is limited by the appearance of the NDR regime.

3.2. Nonlinear transport and the appearance of CMR and CER effects

CMR effects are typically observed at $T < 100$ K in PCMO ($x = 0.33$) films measured in lateral geometry [22]. Lattice disorder and strain can significantly reduce and even entirely suppress the CMR effect [21]. Figure 3(a) summarizes the magnetic field dependence of the overall resistivity $\rho_D$ measured with small constant voltage pulses of $0.08$ V (ohmic regime for all temperatures) in cross-plane geometry. Applying a magnetic field of $B = 9$ T to a typical sample, leads to a CMR transition at about 100 K. This is visible by the strong reduction of resistance at lower temperatures compared to the zero-field cooling/heating cycle. The $B = 9$ T cycle also exhibits a hysteresis between the cooling and the heating, which is characteristic for a phase transition. The hysteresis is not visible in zero-field. With decreasing magnetic field the CMR transition temperature is lowered and the residual resistance at 10 K increases. Below $B = 3$ T, the CMR disappears. Notably, both the $\rho_D(B, T)$ dependence as well as the CMR transition temperature nicely resemble to bulk resistivity $\rho_B(B, T)$ measured in lateral geometry [22], showing the high crystal quality of the PCMO films and that at low $T$ and low $J$, $\rho_D$ is governed by the bulk PCMO contribution, even though $\rho_B(B, T)$ is drastically reduced in the CMR state.

Also in the nonlinear $J$–$U$ regime, the overall behaviour of the cross plane $\rho_D(J, T)$ curves resembles properties obtained in lateral thin film measurements [23]: in particular, CER effects can be induced. $\rho_D(J)$ is successively measured at each temperature step in the current controlled mode (figure 3(b)). For sufficient small current densities the device resistance remains ohmic over the whole temperature range. Increasing $J$ results in temperature-dependent deviations from this ohmic branch until, at high current densities, nonlinear behaviour is observed, even at RT. Therefore, the amplitude of the current-induced resistance drop increases with decreasing temperatures. Notably, splitting of $\rho_D(T, J)$ into different branches successively sets in above a critical pulse voltage of $0.05$ V. This represents the voltage threshold for the crossover from ohmic to nonlinear polaronic transport. Almost no hysteresis between cooling and heating cycle was observed. Below $T \approx 180$ K, the strong $\rho_D$ reduction results in a NDR (see also figure 6(d)). The most apparent CER feature is visible as a
Figure 3. CMR and CER effect in Pt/PCMO/Pt pad devices with $d_{\text{PCMO}} = 300$ nm and 7 µm diameter of the TE. (a) CMR effect in the VS during cooling (large symbols)/heating (small symbols) for different magnetic fields $B$ at a fixed measurement voltage ($U_D = 0.08$ V). The inset shows the corresponding drop of $E_{\text{AD}}$ as a function of applied magnetic field as deduced from the temperature range between 300 and 200 K. The PCMO layer which was post-annealed (973 K for 12 h in air) to improve CMR properties. (b) CER effect in the VS for different $J_D$ during cooling and heating at $B = 0$ T. The different $J$-branches were measured successively at each temperature step. All resistance changes are volatile and independent of the preceding measurements. Below $T \approx 180$ K, the different slope of the resistance branches for higher currents is associated with a NDR (see also figure 6(d)) followed by a step-like resistance drop for $T < 140$ K. The inset shows the corresponding reduction of the apparent activation energy $E_{\text{AD}}$ as a function of current density at $B = 0$ and 9 T, respectively.

step-like resistance reduction below 140 K. This resistance step moves to higher temperatures with increasing $J$.

Application of strong electric fields at different temperatures give rise to quite different $J$–$U$ characteristics which are schematically summarized in figure 4. Experimental examples are shown in figures 5 and 6. At $T > 180$ K, only the ohmic and nonlinear regimes exist. At $T < 180$ K = $T_{\text{NDR}}$, the nonlinear $J$–$U$ evolves into a regime with NDR at sufficiently large $J$. Magnetic fields reduce the overall resistance and giving rise to CMR. The critical voltage $U_{\text{NDR}}$ for the onset of the NDR is shifted to lower values. In addition, for sufficiently large magnetic fields and low temperatures $T < 100$ K, a branch with an NDC ($dJ/dU < 0$) evolves in the $U$–$J$ curve (for experiments, see figures 5(e) and (f)). In contrast to the NDR, the NDC section appears above a critical current density $J_{\text{NDC}}$.

The appearance of NDR and NDC is only accessible in different measurement modes: For NDR, the $J$–$U$ characteristics is uniquely defined for all currents, but not for all voltages. Increasing the voltage above $U_{\text{NDR}}$ leads to a step like current increase until the current limit is reached (figure 5(a)). Conversely, the analysis of the NDC region requires a voltage controlled measurement, because the $J$–$U$ relation is uniquely defined only with respect to the applied $U$. Since for the low temperature with magnetic field applied both NDR and NDC occur, it is not possible to measure the full curve with one measurement mode.
3.3. The resistive switching regime

For a sufficiently large applied current density \( J \geq J_c(T) \approx 10^9\ \text{A m}^{-2} \) deeply in the nonlinear transport regime, RS sets in. It is observable by remanent changes of the resistivity and jump-like features in the \( J-U \) relation. Figure 5 shows the \( T \)-dependent \( J-U \) curves as well as the corresponding relation between resistance and persistent resistance changes \( R_D \) and \( R_{DP} \), respectively. The measurements are performed in pulsed voltage controlled mode and at \( B = 9\ \text{T} \), in order to keep \( R_D(T) \) small enough for the electric measurements at low temperatures. Without these volatile CR effects in the PCMO film, the low temperature device resistance \( R_D \) would be too high to induce RS at moderate values of \( U_D \approx 1-2\ \text{V} \).

The evolution of the \( J-U \) relation under voltage control is shown in figure 5(a) at various temperatures with and without applied magnetic field. With decreasing temperatures \( T < T_{NDR} \approx 180\ \text{K} \), the \( J-U \) characteristic reveals the emergence of a NDR above a critical voltage \( U_{NDR} \) below: the highly nonlinear current increase turns into a step like change which is a result of voltage controlled measurement of the NDR region.

At 300 K (figure 5(b)), a pulsed voltage cycle (\( U_{\text{max}} = 0.75\ \text{V} \)) induces a resistance reduction and a remanent resistance increase from LRS to HRS for \( U_D \geq U_C \approx 0.5\ \text{V} \), where \( U_C \) is the critical voltage for a resistance change \( R_{DP} \) of \( 3\sigma \) above noise. The opposite switching behaviour from HRS to LRS is observed below \(-U_C\). Only for \( T > 200\ \text{K} \), the remanent change is gradual with voltage, resulting in a dependence of \( R_{DP} \) on \( U_D \) with the shape of a parallelogram. For lower temperatures, the NDR leads to a jump-like resistance change, where \( J_D \) jumps into the compliance limit and \( U_D \) is not uniquely defined (figures 5(a) and (c)–(f)).
Figure 5. Temperature dependent resistance and persistent resistance of a 3 $\mu$m sized pad device. The PCMO layer with $d_{\text{PCMO}} = 300$ nm was post-annealed (973 K for 12 h in air) to improve CMR properties. The current was limited to 50 mA. (a) Pulsed current–voltage dependence at different temperatures and $B = 9$ T. Zero-field data at 160 K are shown for comparison. (b)–(f) Pulse voltage dependence of the resistance ($R_D$: black symbols) and the persistent resistance ($R_{DP}$: red symbols) in PS mode of switching at $B = 9$ T and different temperatures. Arrows indicate the sweep directions.

Consequently, a critical voltage $U_C$ is not well-defined, although, there is a trend that higher voltages have to be applied for decreasing temperatures due to the increasing device resistance $R_D(T)$.

This trend is reflected in figures 5(b)–(f), where a systematic temperature evolution of the shape of $R_{DP}(U_D)$ from parallelogram-like to rectangular is observed. In addition, $R_{DP}(U_D)$ entirely changes with decreasing temperature: at $T = 300$ K, the resistance (black symbols)
Figure 6. Temperature dependence of persistent resistance change during current driven cycles at $B = 0$ T for a 3 $\mu$m pad device with $d_{\text{PCMO}} = 300$ nm. The resistance of the LRS at the corresponding temperature (begin of cycle) is subtracted, i.e. $\Delta R = R_{\text{DP}} - R_{\text{LRS}}$. (a) $\Delta R$ in dependence on the pulse voltage. (b) $\Delta R$ in dependence on the applied pulse current density. (c) $\Delta R$ in dependence on the calculated power density, negative values correspond to negative currents. (d) Corresponding $J–U$ characteristics showing the appearance of NDR at low temperatures.

The resistance strongly decreases for increasing $U_D$ at small voltages ($U_D < 0.25$ V), followed by a moderate decrease at higher $U_D$, finally resulting in a jump of $R_D$ at the switching threshold. Below $T_{\text{CMR}} \approx 110$ K, the monotonously decreasing $R_D(U_D)$ turns into an increase of resistance (NDC) (figures 5(e) and (f)). Below $T = 180$ K, the NDR-induced sharp reduction of the resistance is directly connected to the switching between the persistent HRS and LRS states, i.e. the critical switching voltage equals the $U_{\text{NDR}}$ voltage. However, while further decreasing the temperature, $U_{\text{NDR}}$ strongly increases. Below 120 K, the NDC starts to precede the NDR-assisted switching.

In figure 5, the appearance of the NDR with a jump like increase of $J_D$ at decreasing $T$ is directly related to a change of the shape of the $R_{\text{DP}}(U_D)$ curve towards a rectangular like switching. Consequently, the compliance limit is reached for all voltages greater than $U_{\text{NDR}}$, which allows no conclusion about the actual current flow during the switching. Even, the actual $U_D$ value may be strongly affected by the jump in current density and cannot be precisely measured. In order to gain insight into the switching process itself, it is useful to compare the dependence of $R_{\text{DP}}$ on $U_D$ and $J_D$ in voltage and current controlled measurement modes, respectively (figure 6). Because of the NDR at low temperatures (figure 6(d)), the resistances...
changes are only uniquely defined with respect to \( U_D \) at high temperatures (figure 6(a)). Note that at \( T = 300 \text{ K} \), the NDR is only visible in the bulk contribution of \( R_D \) (figure 2(c)), whereas for \( T < 200 \text{ K} \), the NDR shows up in the entire device resistance \( R_D \).

In contrast to \( R_{DP}(U_D) \), the \( R_{DP}(J_D) \) reveals a parallelogram-like shape for the current dependence over a broad temperature range (figure 6(b)). The switching amplitude linearly increases (decreases) with increasing positive (negative) current density (\( \Delta R = (R_{DP} - R_{LRS}) \propto J \)), pointing towards the importance of current density. Note that the HRS (LRS) is not changing during successively reducing current from \( (+-) \) \( J_{max} = 3 \times 10^9 \text{ A m}^{-2} \) back to zero. With decreasing temperature, the slope of \( R_{DP}(J_D) \) and, therefore, the absolute switching amplitude increases. Plotting \( R_{DP} \) as a function of the power density in figure 6(c) almost reproduces the current density dependence; however, \( R_{DP} \) scales very nicely with the power density at different temperatures. The obtained \( \Delta R_{max} \) differs for different \( T \) because of the required increasing \( U_{max} \) at lower \( T \). This is pointing towards a possible role of Joule heating in assisting the processes involved in RS.

3.4. Modification of electric transport properties by resistive switching

In order to determine the effect of RS on the polaronic transport properties below the switching threshold, we have applied voltage cycles to our samples at 300 K and measured the \( R_D(T) \) dependence of the different formed states (VS, HRS and LRS). The resulting changes in the polaronic transport compared to the VS are analysed by determination of the activation energy for thermally activated polaron hopping from \( R_{DP}(T) \) measurements at \( B = 0 \) and \( 9 \text{ T} \), and by studying the induced changes in the CMR effect (figure 7).

Before we start with the analysis of the switching induced changes in electric transport, we want to introduce the presence of two different switching modes with different sign of \( \Delta R^* \) at different \( U_D \) amplitudes (figure 7(a)). This finding has been already reported in [19] and can be either attributed to the switching processes at the two involved interfaces or to the presence of two different switching mechanisms. The RS with small amplitude of \( \Delta R^*/R_{LRS} \leq 20\% \) and without any degradation is defined as ‘positive switching’ (PS), since positive voltages lead to increase of remanent resistance (LRS \( \rightarrow \) HRS). Applying \( U_{max} \geq 1 \text{ V} \) drastically increases the switching amplitude up to \( \Delta R^*/R_{LRS} \approx 1000\% \), and also changes the switching polarity: Since in this voltage regime negative voltages lead to an increase of the remanent resistance (LRS \( \rightarrow \) HRS), the switching is now defined as ‘negative switching’ (NS). In this NS mode, small dip/rise features before the pronounced transitions demonstrate the co-existence of this mode with the small amplitude PS mode at lower voltages. It is possible to restore the PS mode simply by returning to voltage cycles with smaller amplitude (\( U_{max} = 0.75 \text{ V} \)). However, this ‘restored PS’ (R-PS) mode gives rise to a permanently shifted low-resistance state compared to the initial PS mode (figure 7(b)) indicating permanent, non-reversible changes. Increasing the voltage amplitude towards 1 V reestablishes the NS switching mode again. A further increase of voltage amplitudes \( U_D \) above 1 V increases the switching amplitude without further changes of switching mode. Applying \( U_{max} = 1.5 \text{ V} \) leads to a more pronounced NS. For convenience, we define this switching regime as NS*, indicating that it was established after performing a sequence of PS \( \rightarrow \) NS \( \rightarrow \) R-PS switching cycles.

Figure 7(c) reveals the temperature dependence of \( R_{DP} \) in the VS, the LRS (formed by negative voltages up to \( U_{max} = -0.7 \text{ V} \)) and the HRS (formed by positive voltages up to \( U_{max} = +0.7 \text{ V} \)) in the PS regime. Switching parameters and activation energies determined from

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Figure 7. Field and temperature dependence of persistent resistance states of a pad device with a diameter 3 µm with $d_{\text{PCMO}} = 300$ nm. Colours represent same switching modes/states. (a) Pulse voltage dependence of $R_{\text{DP}}$ at 300 K and $B = 0$ T in different switching modes after establishing stable voltage cycling between HRS and LRS. (b) Resistance shift between initial PS and restored R-PS mode. (c) Temperature dependence of VS and LRS/HRS resistance of the initial PS mode at 9 T. (d) Temperature dependence of LRS in different switching modes. Also the HRS of the NS$^*$ is shown. For definition of the various switching modes, see text.

$R_D(T)$ are summarized in table 1 (see discussion for details). The relation $R_{\text{HRS}} > R_{\text{VS}} > R_{\text{LRS}}$ holds over the whole temperature range in the PS mode. In comparison to the VS, the HRS reveals a slightly higher activation energy and $T_{\text{CMR}}$ is shifted to lower temperatures. In the LRS, a small reduction of the activation energy and a shift of the transition temperature to higher temperatures are observed. In contrast to the initial PS (and the R-PS) mode, pronounced switching in the NS$^*$ mode drastically changes the temperature dependence of $R_{\text{DP}}$ (figure 7(d)): although the LRS of the PS and the restored R-PS mode strongly differ in magnitude of resistance, $T_{\text{CMR}}$ and $E_A$ are quite similar. Remarkably, at RT, the LRS of the NS$^*$ mode reveals nearly the same resistance as the R-PS low-resistance state, but the activation energy is much higher and the CMR is completely suppressed. The HRS state of the NS$^*$ mode has an extremely high resistance value, but the CMR is reestablished and the activation energy is reduced even below the VS value. Note that these changes of CMR and $E_A$ are reproducible, i.e. another switching cycle within the NS$^*$ mode to the LRS reproduces the LRS–NS$^*$ curve in figure 7(d),

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Table 1. Summary of polaronic properties of various resistance states presented in figure 7. All resistance states were set at 300 K. PS corresponds to the initial positive switching, NS* to a negative switching with high switching ratio and R-PS to the restored PS-Mode. The resistance states were established by the switching sequence: virgin state VS → PS → NS (U_{\text{max}} = 1 V → R → PS (U_{\text{max}} = 0.8 V) → NS*. U_{\text{max}} is the maximum voltage applied to establish the resistance state and \( \rho_D \) is the device resistivity at 9 T and 300 K. \( \rho_0D \) is the pre-factor and \( E_{\text{AD}} \) the activation energy at 9 T deduced from the temperature dependence of \( \rho_D \) in the range from 300 to 200 K according to equation (1). \( \Delta E_A \) is defined as \( E_{\text{AD}}(0 \text{T}) - E_{\text{AD}}(9 \text{T}) \). The CMR transition at 9 T is characterized by the temperature \( T_{\text{CMR}} \) (resistance maximum) and the resistance ratio \( R_D(10 \text{K})/R_D(300 \text{K}) \).

| Final resistance state | \( U_{\text{max}} \) (V) | \( \rho_D \) (300 K) \( \times 10^{-3} \Omega \text{ m} \) | \( \rho_0D \) \( \times 10^{-8} \Omega \text{ m K}^{-1} \) | \( E_{\text{AD}} \) (meV) | \( \Delta E_{\text{AD}} \) (meV) | \( T_{\text{CMR}} \) (K) | \( R_D(10 \text{K})/R_D(300 \text{K}) \) |
|-----------------------|----------------|------------------|----------------|----------------|----------------|----------------|----------------|
| VS                   | 3.54           | 9.0(2)           | 126.3(4)       | 14.6(6)       | 104            | 7.0            |                |
| PS–HRS               | +0.7           | 3.92             | 9.6(1)         | 127.3(4)      | 13.9(6)        | 108            | 5.9            |
| PS–LRS               | -0.7           | 3.24             | 8.7(2)         | 124.9(3)      | 15.2(6)        | 102            | 12.2           |
| RPS–LRS              | -0.8*          | 10.46            | 26.3(5)        | 127.0(4)      | 11.2(8)        | 97             | 8.4            |
| NS*–LRS              | +1.5           | 13.19            | 10.7(5)        | 154.9(4)      | 9.9(8)         | (< 10)         | (> 2000)       |
| NS*–HRS              | -1.5           | 153.02           | 744 (14)       | 109.7(4)      | 4.7(9)         | 70             | 30.2           |

with the same \( E_A \) values and absence of the CMR features as during the first NS* cycle. In general, independent of the switching mode, positive voltage increases \( E_A \) and reduces \( T_{\text{CMR}} \).

4. Discussion

The ranges of the observed three different electric transport regimes in Pt–PCMO–Pt devices, i.e. ohmic, nonlinear and RS (figure 4), can be summarized as follows. The ohmic regime with a linear \( J–U \) characteristics shows up for small voltages \( U \leq 0.05 \text{ V} \) and small current densities \( J \leq 10^8 \text{ A m}^{-2} \) at RT and is well described by equation (1). Whereas the voltage threshold for the ohmic regime is rather temperature independent, the current density threshold drops with decreasing \( T \) due to increasing device resistance \( R_D(T) \). RS regime sets in above a temperature dependent critical current density of the order of \( J_c \approx 10^9 \text{ A m}^{-2} \) at RT. The threshold current density drops down by approximately one order of magnitude with decreasing \( T \) from 300 to 100 K. The transport behaviour in the intermediate regime between ohmic regime and switching behaviour is characterized by a nonlinear \( J–U \) characteristic which is due to the polaronic \( J–U \) relation (equation (2) and figure 2(c)). At sufficiently large voltages/currents, but still below the switching threshold, Joule heating can induce a NDR: \( R_D(T) \) decreases with increasing device temperature. Consequently, in bias controlled measurements, Joule heating increases the current density until a further resistance decrease does not generate additional heating power (self-stabilization). The appearance of a NDC in the CMR regime (in strong magnetic fields at low \( T \)) is related to the break-up of the electrically conducting ferromagnetically (FM) ordered state by highly driven polaron states and related Joule heating.
4.1. Transport properties below the switching threshold

Experimentally, the device electric transport reveals properties which are well known and commonly attributed to the interplay of polaronic mechanisms and magnetic double exchange interactions in PCMO ($x = 0.33$) in lateral geometry: the electric conduction is well described by the hopping mobility of small polarons, and, at temperatures below $T_{\text{CMR}} \approx 100$ K at $B \geq 3$ T, devices with sufficiently low amount of lattice disorder reveal CMR transitions. In particular, the temperature dependence of $R_D(T, B)$ (ohmic regime) in figure 3 in the range $200 \leq T \leq 300$ K can be fitted by equation (1). This is well in the applicability range of the adiabatic Holstein model of thermally activated hopping of small polarons [13] for $T > \Theta_D/2$, where $\Theta_D \approx 300$ K represents the Debye temperature. The resulting apparent activation energies $E_A$ coincide with the bulk values of about 135–150 meV observed in lateral measurements of epitaxial films ($x = 0.33$); see table 1 and [14].

This agreement is quite remarkable, since the device resistance is composed of the bulk and the interfacial contributions and $E_A$ is very sensitive on subtle changes in the slope of $R_D(T)$. According to the result of the series circuit, equation (3), we write

$$\rho_D(T) = \rho_{0B} T e^{\frac{E_{\text{AD}}}{k_B T}} \frac{d_{\text{eff}}}{A} = \rho_{0B} T e^{\frac{E_{\text{AD}}}{k_B T \text{PCMO}}} \frac{d_{\text{PCMO}}}{A} + \frac{\delta_1(T)}{A},$$

where $d_{\text{eff}}$ represents the effective thickness of the PCMO film including interfacial regions of the two metal electrodes and

$$E_{\text{AD}}(B, J) \equiv k_B \frac{d \ln \left( \frac{R_D(B, J)}{T} \right)}{d \left( \frac{1}{T} \right)}$$

is the apparent activation barrier associated with the device resistance $R_D(T)$. The observation, that $E_{\text{AD}}$ is in the same range of values as for bulk samples $E_{\text{AB}}$, allows us to derive some conclusions about the temperature dependence and nature of the interface resistance $\delta_1(T)$ in the VS.

At RT and small electric fields the resistance contributions of the interface and the bulk are of same order (figure 2). If the temperature dependence of interfacial and bulk contributions (for temperatures between 300 and 200 K) would be quite different, the apparent activation energy $E_{\text{AD}}$ deduced from overall device resistance should significantly deviate from the intrinsic PCMO value. Assuming for example that the charge transfer across the interface is controlled by a thermally activated interfacial process with an interface resistance of the form

$$\delta_1(T) = \delta_{0I} T e^{\frac{E_I}{k_B T}},$$

and, that $E_I \gg E_{\text{AB}}$ of bulk PCMO, the CMR transition at low temperatures would not be visible due to the allower dominance of the interfacial contribution. In contrast, the assumption of $E_I \ll E_{\text{AB}}$ or even a constant or ‘metal-like’ temperature dependence of $\delta_1(T)$ would lead to a strongly reduced apparent activation energy of the device. This gives rise to the conclusion that $E_I \approx E_{\text{AB}}$ at least in the temperature range $300 \geq T \geq 200$ K of the applicability of the Holstein model and at low current densities.

The statement that the polaronic mobility controls the interface resistance also holds in the nonlinear regime. For sufficiently low $J$, the nonlinear current–voltage dependence of polarons is given by equation (2). This formula can be approximated by equation (1) through the introduction of the apparent activation energy $E_{\text{AD}}(J)$. The quality of the fits of $R_D(T)$ for different $J$ remains high for all currents. The apparent activation energy thus represents an
average over film and interface regions with different local electric field and decreases from about 140 meV in the ohmic regime to 50 meV in the nonlinear regime (inset of figure 3(b)). It is important to note, that both the magnitude and the current density dependence of $E_{AD}(J)$ is not very different from that one obtained in lateral (in-plane) four point measurements in epitaxial PCMO films on SrTiO$_3$ single crystals. We have shown by the analysis of bulk and interface contributions to the $U$–$J$ characteristics in figure 2(c) that the ratio of interface to bulk resistance increase from $Q = 0.4$ to 2 with increasing $J$. Consequently, despite of the larger electric field at the PCMO–Pt interfaces compared to the PCMO film, and despite of the dominance of the interface resistance over bulk resistance at high $J$ ($Q > 1$), $E_{AD}(J)$ shows the same characteristics as for bulk transport.

A possible reason for the astonishingly similar polaronic behaviour of the bulk and interface contributions is the specific nature of the charge injection across the PCMO–Pt interface: based on the workfunctions of $W_{PCMO} = 4.89$ eV and $W_{Pt} = 5.65$–6.35 eV at 300 K [24], the formation of electro-chemical equilibrium at the PCMO–Pt interface would give rise to positive band bending in PCMO (figure 8(a)). Due to the high carrier doping for $n_{PCMO} = 6.4 \times 10^{27}$ m$^{-3}$ ($x = 0.3$) and the large dielectric constant $\varepsilon \approx 30$ [25], the electronic screening length of $l \approx 0.2$–0.7 nm in PCMO is very small. The positive band bending causes an ohmic contact resistance: Under application of an external potential (figure 8(b)), the built-in potential of the interface with negative bias is increased, whereas the built-in potential for the interface at positive bias is decreased. Consequently, under an applied electric bias, electron run downhill across that interface with increased built-in potential, whereas the barrier for uphill interface charge transfer is decreased.

Although the contact resistance is of ohmic nature, charge transfer across the interface is not just given by the propagation of electrons across the interface. Moreover, charge injection requires the transfer of quasi-free electrons in the metal electrodes into the oxide, where they must be converted into hole-type small polarons. Electron injection from the electrode at negative potential into the oxide thus take place via annihilation of electrons with polaron hole states. The injection rate must then be limited by the hopping transport of polarons to the annihilation region near the interface. Conversely, the emission of electrons from the oxide into the electrode at positive potential requires the generation of polaron type electron–hole pairs at the interface at a rate which may again be limited by the hopping mobility of hole-type polarons which have to move away from the interface. The suggestion that the interface resistance is controlled by polaron generation and annihilation and thus by the electric field dependent hopping mobility of the polarons is further supported by the consideration of the average drift velocities of electrons and polarons in the Pt and PCMO, respectively. Since the charge density of Pt ($n_{Pt} = 1.6 \times 10^{28}$ m$^{-3}$) is almost twice of that one of PCMO at $x = 0.3$, the continuity of the current density at the interface in the stationary state requires that the drift velocity of the carriers in PCMO must be almost double of that one of Pt. Thus, in stationary states, polaron mobility should represent the bottleneck for the interface resistance and thus explains its polaronic nature.

4.2. Electric transport near the switching threshold

Our conclusion that interface and bulk contributions must be both governed by polaronic transport mechanisms with similar activation barriers $E_I \approx E_{AB}$ only applies under the constraint that the interface resistance is of the same magnitude or larger than the bulk resistance.
Figure 8. Schematics of the interfacial band bending based on the different work functions of Pt and PCMO (see text). (a) Electro-chemical equilibrium between the quasi-free electrons in the metallic electrodes and the hole type polarons in the 3d $e_g$ conduction band of PCMO. (b) Schematic change of the band structure due to an applied bias, leading to an ohmic contact resistance. The charge transfer across the interface is governed by the injection of electrons (1) and subsequent electron–hole recombination or (2) by emission of electrons based on electron–hole pair generation. The rate of both processes may be limited by the hole polaron motion at near interface areas and thus is governed by the bulk hopping mobility of small polarons.

For temperatures below 200 K the evolution of $Q(T,J)$ might change. Even small differences between $E_I$ and $E_{AB}$ would lead to increasingly large differences in the temperature dependence of $R_I$ and $R_B$ at very low $T$. Basically, two details imply that the bulk contribution starts to dominate at low temperatures and high current densities: In this regime, the overall device resistance reveals a NDR (figure 6(d)), which looks similar to the pure bulk NDR at 300 K which is separated out in figure 2(c). In addition, under an applied magnetic field we observe the resistance reduction due to the CMR effect. Below $T_{CMR}$ ($\approx 100$ K), both a NDC and a NDR appears in the $U$–$J$ characteristics (see figure 5(f)). In the CMR regime, the increase of resistance with increasing $J$ may be a result of a ‘break up’ of the FM state by the applied current. The CMR effect and its reduction by a sufficiently large current density are therefore
also considered as bulk effects rather than interface effects, because the FM state requires long range order. Since the interface resistance is controlled by charge injection and thus by the PCMO polaron mobility, it is evident that $\delta_I$ follows $\rho_B$ in the CMR transition.

At least at 300 K and for very high current densities (switching regime), the voltage drop and therefore the electric fields are most prominent at the interfaces, which make them a plausible location for the processes involved in RS. The mechanism leading to remanent resistance changes seems to be rather current or even power density than voltage driven (figure 6). This is most prominent at 165 K, where due to the NDR the current density is not proportional to the applied voltage. The switching only takes place above $U_{\text{NDR}}$, where the applied voltage is reduced and the current density jumps into the compliance limit. Therefore, the ‘break-down’ of the bulk contribution $\rho_B$ then gives rise to an increase of the current density and, consequently, a shift of the voltage drop from the film to one of the interfaces, thus enabling RS. Since at low temperatures, RS only takes place in the NDR regime, this indicates the presence of interface type switching topology also at low temperatures. The scaling of $\Delta R$ with the power density (figure 6(c)) points to a possible role of Joule heating, which may assist the electronic and microstructural changes involved in the switching process.

4.3. Switching induced modifications of polaron transport properties

We have shown (figure 7) that the modifications of the electronic and structural properties of the interfaces and films by pronounced RS have a strong impact on the electric transport properties below the switching limit. Remarkably, depending on the switching mode, the polaron activation energy as well as the CMR effect can be modified significantly. However, even the strong modifications which lead to the HRSs in NS* mode still exhibit small polaron hopping conductivity and can be well fitted with the TAP model equation (1); see table 1.

There are three well-established mechanisms which can cause non-volatile changes in polaron mobility: changes of the doping level, changes of the disorder potential and CO/disorder transitions. Point defects can modify the disorder potential, the Mn valence state, the resulting carrier concentration and also the strength of electronic correlations, such as the electron–phonon interaction [26, 27]. CO/disorder transitions can be induced by electric stimuli at interfaces even at RT [7].

The small amplitude PS around the VS (figure 7(c)) has only minor influence on the high temperature branch of $R_D(T)$. The switching mechanism in this switching mode is characterized by an increase of remanent resistance (PS–HRS) for positive currents. This is accompanied by a slight increase of the activation energy $E_{\text{AD}}$, a decrease of the magnetic field dependence $\Delta E_{\text{AD}}(B)$ and an increase of the pre-factor $\rho_{\text{BD}}$. The larger ratio of $R_D(10 \text{ K})/R_D(300 \text{ K})$ and the reduced $T_{\text{CMR}}$ reflect a significant deterioration of the CMR effect. These results are compatible with two different mechanisms: reversible changes of disorder at or near an interface region as well as a modification of polaron mobility due to polaronic charge ordering at the interface. In the disorder scenario, the increase of $\rho_{\text{BD}}$ and the slight increase of $E_{\text{AD}}$ may be caused by the formation of disorder at one of the interfaces, giving rise to an increase of $\delta_{\text{O}}$ and $E_1$ in the HRS (assuming that the interface resistance dominates). Alternatively, in the CO scenario, the emission of electrons and related dynamic hole accumulation at one of the interfaces may lead to charge ordering [7] which also increases $E_1$ as well as $\delta_{\text{O}}$. In contrast, the reduction of $E_1$ as well as $\delta_{\text{O}}$ in the PS–LRS either indicates the healing of disorder, or the improvement of polaron mobility due to charge injection induced attenuation of CO. The CO scenario is
supported by the observation of the absence of any formation process, often found in electromigration controlled mechanisms [11]: LRS as well as HRS can be equally formed starting from the VS, just depending on the polarity of the stimulation. Since a change in CO affects the CMR transition temperature, the observed shift of $T_{CMR}$ in PS switching is in agreement with the CO scenario.

For larger switching amplitudes in the NS* mode, the effect of the switching induced LRS and HRS on the $E_{AD}$ and CMR are much more pronounced. Positive currents lead to a NS*–LRS with a strongly increased $E_{AD}$. In addition, the pre-factor $\rho_{0D}$ is strongly reduced and a smaller but still significant magnetic field dependence of $\Delta E_{AD}(B)$ is observed. The CMR induced ‘metal like’ temperature characteristics with a decreasing low temperature $R_{D}(T)$ is entirely suppressed. In this switching mode, the separation between an interface resistance and a bulk resistance, where only the interface contribution changes, seems to be questionable. Pronounced electro-migration of oxygen ions towards the interface may simultaneously cause a strong drop in the interface pre-factor $\rho_{0D}$ and a significant increase of the point disorder in the bulk of the PCMO film. In contrast, the NS*–HRS is characterized by an increase of $\rho_{0D}$, a strong drop of $E_{AD}$ and the preservation or even reestablishment of the CMR. This clearly points to the formation of disorder at the interface combined to a decrease of disorder in the bulk PCMO. In contrast to the PS, a first initialization by a negative cycle is required for the formation of HRS. This generates a permanent resistance shift which is also consistent with an electro-migration mechanism.

It is evident that PS and NS are related to two different switching mechanisms. The two mechanisms can either coexist at a single interface or can be related to two opposing interfaces. The crossover between PS and NS is related to a change in pre-dominance of the two involved processes. Assuming that the resistance change of both mechanisms mainly takes place at the top electrode interface, the NS mode is consistent with a mechanism, where the change of the oxygen vacancy distribution by electro-migration is involved. In contrast, the PS is consistent with changes in interfacial disorder as well as CO/disorder transitions nucleating at the interface. Switching at the top interface is supported by the geometric configuration, where Joule heating induces a temperature asymmetry of the two interfaces due to improved heat transport at the lower electrode.

5. Conclusions

We have motivated a serial resistance model for the electric transport in Pt/PCMO/Pt devices. The two components were identified as interface and bulk contribution with comparable magnitude in the top-to-bottom geometry at RT. Typical activation energies and CR features reveal a polaronic transport system with comparable properties in both, bulk and interface contribution. The CR features can be utilized to apply sufficient current densities as a driving force for remanent RS also at low temperatures down to 10 K. NDR and the scaling of the obtained resistance change with the power density of the pulses indicates presence of strong Joule heating close to the switching regime which can significantly assist polaronic mobility and electromigration. On the other hand, remanent RS changes the polaronic transport system and therefore the CR properties. The actual change depends on the two different switching regimes and their corresponding switching modes PS and NS, respectively. They seem to be a result of two different mechanisms. Whereas PS can be attributed to interface induced modifications of the activation energy $E_{AD}$ and the pre-factor, the stronger NS clearly modifies the bulk
properties of the PCMO film and can entirely erase and reestablish the CMR effect. Generally all states are governed by polaronic transport which can be well described by the TAP model (equation (1)) in the appropriate temperature range.

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