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Resistive Switching in Perovskite-Oxide Capacitor-Type Devices

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Resistive switching effect was demonstrated in the Ti/Pr₀.₇Ca₀.₃MnO₃ (PCMO)/LaNiO₃/Ti top-down device structure. A high resistance state was activated by a forming process. Hysteretic current–voltage (I–V) characteristic was observed by applying potential differences in the order of 5 V across the electrodes. I–V characteristics with different combinations of top and bottom electrodes suggested that the forming process changed the interface between the oxides and Ti electrodes, with the active region for resistive switching located at the Ti electrode/PCMO interface region. Such results show the possibility of high-density and nonvolatile memory applications based on the resistive switching effect.

Index Terms—Nonvolatile memories, Pr₀.₇Ca₀.₃MnO₃ (PCMO), resistive switching.

I. INTRODUCTION

Resistive switching effect is hailed as one of the candidates for the next-generation nonvolatile memories [1]. Upon the application of a voltage pulse, the sample resistance can be changed and retained. This effect has been manifested in various materials and device geometries [2]–[4]. Some of the advantages of the effect include the fast writing time (<10 ns) [5], low operating voltage [6], and potentially high data storage densities [7].

Pr₀.₇Ca₀.₃MnO₃ (PCMO), for example, is one of the promising materials, which shows resistive switching in thin-film device structures [8]. Switching ratio over 3000% and switching voltage below 2 V have been achieved [6], [8], [9]. However, further advancement of the performance in such devices requires thorough understanding of the working mechanism, which is still under debate [10], [11]. A few schemes have been proposed, involving either bulk or interface effects, with the interfacial contribution considered to be more important in perovskite-based resistive switching devices [4], [12]–[14]. Some of the most common explanations include the presence of trap states within the Schottky barrier, trapped-charges-induced space-charge-limited current, as well as formation of oxides at the electrode/oxide interfaces [4], [9], [14]–[17].

In this paper, we study the current–voltage (I–V) characteristics and resistive switching behavior of epitaxially grown PCMO with LaNiO₃ (LNO) and Ti as bottom and top electrodes, respectively. By investigating the I–V characteristics for various electrode combinations, we argue that the active region for resistive switching is located at the Ti/PCMO interface. The highly localized nature of the switching effect highlights the possibility of simplifying the device fabrication process using a common bottom electrode.

II. EXPERIMENT

Thick (200 nm) epitaxial LNO layers were grown by pulsed laser deposition on LaAlO₃ (LAO) substrates at a temperature of 650 °C and oxygen pressure of 150 mtorr [18], [19]. The laser pulse energy was around 250 mJ, with a pulse repetition rate of 5 Hz. A 100-nm-thick PCMO film was then deposited on the LNO layer through a stainless steel shadow mask at the same temperature and oxygen ambient, with a laser pulse energy of 200 mJ. Afterwards, the epitaxial layers were cooled down to room temperature at a rate of 10 °C min⁻¹ under the same oxygen pressure. The chamber was then pumped down to 3 × 10⁻⁵ torr, before the Ti electrodes with diameter 100 μm were defined and deposited on top of the PCMO using another shadow mask.

Structural analyses of the samples were performed by X-ray diffractometry (XRD), and electrical measurements (I–V characteristics and resistive switching measurements) were done at room temperature by a Keithley 2400 sourcemeter. A current passing from the top Ti electrode through PCMO into the LNO layer was defined as a positive current.

III. RESULTS AND DISCUSSION

A. Structural Characterization

Fig. 1 shows the θ-2θ scan of a PCMO/LNO sample. The PCMO (002) and LNO (002) peaks are basically overlapping with one another. The rocking curve of the PCMO/LNO film (upper inset, Fig. 1) at the (002) peak shows the oxide layers are textured with a full-width at half-maximum (FWHM) of 0.67°. The small FWHM shows that the PCMO film deposited on LNO has good crystallinity. φ-scan (lower inset) further confirms the epitaxial cube-on-cube growth of the multilayer on the LAO substrate.

B. Electrical Characterization

Resistive switching measurements were performed with the circuit shown in Fig. 2(a). Reproducible changes in sample resistances, after the application of voltage pulses, are shown in Fig. 2(b). The measurement procedure is as follows. After applying a pulse at +4.5 V for 1 ms, the sample resistance...
Fig. 1. XRD pattern of a PCMO/LNO/LAO device. Upper inset: \( \omega \)-scan of the PCMO thin film. Lower inset: \( \varphi \)-scans of (a) LAO substrate and (b) LNO/PCMO film.

was measured with a bias of \(-2\) V. Subsequently, a \(-4.5\) V pulse was applied to switch the sample to the low resistance state (LRS), and the resistance was measured again at \(-2\) V [see inset of Fig. 2(b) for the voltage profile during the measurement cycle]. Switching properties were stable over at least 40 switching cycles, and an averaged switching ratio of 230% was obtained, a resistance variation that is easily observed by conventional means of measurements.

It should be pointed out that the forming process is needed to prepare the device for resistive switching applications [18], [20], [21]. During the forming process, a voltage of \(+7\) V was applied across a particular device, meaning that the electric current passed from the top PCMO to the bottom LNO layer. Initially, the sample exhibited a relatively low resistance. When the voltage was ramped up \(+6\) V, the resistance suddenly increased to the order of a few k\(\Omega\). Afterward, the resistance of the sample was kept at the same order of magnitude and did not return to its initial state. After forming, an asymmetric and hysteretic \(I-V\) was observed, with a sharp current increase occurring in the negative voltage bias regime [Fig. 3(a) black square line (Ti\(_1\)-Ti\(_I\))]. The bias voltage for resistance switching to occur was about \(-4\) V in this case. This confirms that, in our resistance switching measurements, \(\pm 4.5\) V was sufficient to switch the sample between high resistance state (HRS) and LRS.

A simple analysis of the top-down geometry device can be made by considering a model with three interfacial (Ti/PCMO, PCMO/LNO, and LNO/Ti\(_I\)) and two bulk (PCMO and LNO) resistors connected in series. Various works on perovskite-based resistive switching devices suggested that switching occurs predominantly at interfaces [13], [18], [20], [22]. We have previously studied planar perovskite-based resistive switching devices, and have eliminated the bulk contribution to the switching effect [19]. Thus, there are three interfaces, which may contribute to the resistive switching in our top-down geometry devices.

To locate which interface(s) was modified during the forming process, electrode-swapping measurements were performed. During such measurements, the forming process was conducted on a fixed pair of electrodes Ti\(_I\) (on the PCMO layer) and Ti\(_I\) (on the LNO layer) (Fig. 3), with the current path be represented by Ti\(_I\)/PCMO/LNO/Ti\(_I\). Subsequently, \(I-V\) characteristics were measured by fixing Ti\(_I\) on PCMO while switching between two Ti electrodes on LNO (Ti\(_I\) and Ti\(_{II}\)). The results for such measurement procedures are shown in Fig. 3(a). For the measurement with the Ti\(_I\)/PCMO interface paired with LNO/Ti\(_I\) (Process 1), the junction shows hysteretic \(I-V\) behavior after the forming process. After that, connection to Ti\(_I\) was fixed while the bottom electrode was switched to Ti\(_{II}\) (Process 2). In Process 1, the interfaces Ti\(_I\)/PCMO, PCMO/LNO, and LNO/Ti\(_I\) were involved, the last of which was replaced by LNO/Ti\(_{II}\) in Process 2. If the change induced by forming process mainly occurred at LNO/Ti\(_I\), \(I-V\) characteristics should be different in these two processes, as LNO/Ti\(_I\) did not experience forming process. The present result suggests that the change induced by the forming process did not occur at the LNO/Ti interface.

\(I-V\) characteristics for swapping the top electrodes (i.e., measuring with different top electrodes Ti\(_I\) and Ti\(_{II}\) with fixed bottom electrode Ti\(_I\), Processes 3 and 4) were also obtained [Fig. 3(b)]. Note that no previous measurements have been performed on Ti\(_{II}\) before the swapping test. Similar to the above analysis, if the Ti/PCMO interface was modified by the forming process, the Ti\(_{II}\)/PCMO and LNO/Ti\(_I\) interface pair should not show hysteretic behavior but should be observable...
in the Ti$_1$/PCMO with LNO/Ti$_1$ interface pair. This was actually observed at this paper. Owing to these results, it can be concluded that the changes mainly occurred at Ti/PCMO interface in the forming process. It can also be concluded that Ti/PCMO interface contribute to the switching effect in the formed devices, as the forming process is necessary to activate the switching behavior.

As mentioned previously, the forming voltage must be positive, in which the current passes from the top Ti electrode through PCMO into the LNO layer. Fig. 4 shows the $I$–$V$ characteristics of the same device structure after forming with a negative bias of $-9$ V. In contrast with the case of positive bias-formed devices, no clear resistive switching effect is observed; attempts of sweeping over wider voltage ranges did not have these problems. Together with the simplicity of data retrieval and read/write operations, we suggest that such a memory scheme has much potential for future high-density nonvolatile memory applications.

IV. CONCLUSION

PCMO-based top-down geometry resistive switching devices with Ti electrodes were studied. Ti/PCMO/LNO/ LAO resistive switching devices were obtained after the forming process. Experiments with different electrodes suggested that the resistive switching region was located at the Ti/PCMO interface, and the effect was explained through the oxidation and dissociation of interfacial TiO$_x$.

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