Interface analysis of resistive switching manganite-based thin film heterostructures by hard x-ray photoelectron spectroscopy

R. Dittmann, F. Borgatti¹, F. Offi², C.-W. Park, A. Herpers, C. Lenser, C.M. Schneider, G. Panaccione²

Peter Gruenberg Institute (PGI-7) and JARA-FIT Forschungszentrum Juelich GmbH, 52425 Juelich, Germany.

¹CNR – Istituto per lo Studio dei Materiali Nanostrutturati, via Piero Gobetti 101, 40129 Bologna, Italy
²CNR Istituto Officina dei Materiali (IOM), Laboratorio TASC, S.S.14, Km 163.5, I-34149 Trieste, Italy
³CNISM and Dipartimento di Fisica, Università Roma Tre, Rome, Italy

Perovskite manganites are particularly promising for the development of non-volatile Resistance Random Access Memories (RRAMs), owing to their largely tunable electric and magnetic properties [1,2]. Moreover, high and low resistive state currents of several manganites films scale with the electrode area, which might be advantageous for circuit design since it offers another degree of freedom to adjust the device parameters [3]. It is widely recognized that the bipolar RS behaviour exhibited by manganite compounds is most frequently connected with voltage-driven oxygen vacancy movement, therefore relevant redox processes may occur at the electrode/oxide interfaces [4,5]. The chemical states of the boundary regions can differ significantly from the bulk and are susceptible of a crucial role for the establishment (or the enhancement) of the RS since the initial electro-forming process. This treatment, consisting of strong voltage stress application, is evenly essential to set and/or improve the reproducibility of the RS also for perovskite compounds exhibiting native switching behaviour. Therefore the detailed identification of the chemical states at the interfaces and their relationship with electroforming is a key question. In this experiment we have approached this topic for Pt/Ti/Pr₀.₅Ca₀.₅MnO₃/SrRuO₃ layered heterostructures (Pt/Ti/PCMO/SRO), formed in different resistive states, by exploiting the bulk sensitivity of the core-level hard x-ray photoemission spectroscopy (HAXPES) to perform nondestructive studies of the top Ti electrode and the underlying PCMO oxide layers. The HAXPES measurements were performed at the P09 beam-line. The experimental geometry was chosen to maximize the bulk sensitivity, with the angle between the incident x-ray beam and the electron analyzer set to 90°, and the x-ray beam grazing incidence at 2° on the samples. The photon energy was set at 7.4 keV and was periodically verified by measuring the Fermi edge spectrum of a reference Au sample. The overall resolution was 0.35 eV. All the measurements were performed at room temperature. Due to the large footprint of the x-ray beam, single devices were not suitable for HAXPES measurements and therefore device arrays were fabricated, consisting of a large number of 50x50 μm² pads organized in stripes about 7 mm long and 0.8 mm wide, where every stripe consist of pads in the same resistive state. The spacing between the pads was about 10 μm. Typical thickness of the layers for the probed systems is 4 nm (Pt), 10 nm (Ti), 20 nm (PCMO), 30 nm (SRO). The photoelectron emission from the buried regions of interest is ensured by the large electron inelastic mean free path (IMFP) typical of the hard x-ray excitation regime, of the order of 8 nm. The most important experimental results are summarized in Fig. 1. The Ti 2p spectra for the top Ti electrode layer, shown in Fig. 1(a), have been detected for samples in the as-prepared state (“pristine”), and in three resistive states obtained by adopting slightly different electroforming protocols. Because of the partial overlap of the Ti 2p₁/₂ with the Ru 3p₃/₂ peak, only the spectral region of the Ti 2p₃/₂ components is clearly distinguishable and exhibits two distinct features at about 454 eV and 459 eV
which are associated to Ti\(^0\) (metallic) and Ti\(^{4+}\) ion valence states, respectively. The relative intensity of these two peaks is progressively modified, demonstrating the strong sensitivity of the HAXPES spectra to changes of the Ti chemical states due to the electroforming process. The lineshape comparison of the Ti 2p spectra, reported in Fig. 1(b), suggests that progressive formation of TiO\(_2\) through the diffusion of oxygen ions from the PCMO within the Ti layer is achieved following the sequence of electroformed states from #1 to #3, which occurs correspondingly to the increase of the device resistance. Moreover, the detailed fit analysis of the Ti 2p spectra (not shown here) indicates very clearly that both spin-orbit components include intermediate valence terms, thereby confirming that even for the as-prepared system there is a large chemical interaction with the underlying PCMO. Concerning the PCMO elements, the most noticeably spectral changes have been observed for the Mn2p spectra, shown in Fig. 1(c) together with the spectrum of bare PCMO reference sample. The chemical shift occurring for the Mn ions of all the devices is interpreted as the change of the Mn\(^{4+}\) species to lower valence states (Mn\(^{3+}\)) due to the release of surrounding oxygen atoms during the growth of the Ti top layer, in agreement with the Ti 2p results. These results demonstrate that we have succesfully provided a complete characterization of the chemical states for the Ti top electrode and the Ti/PCMO buried interface of resistive switching devices. It turns out that the progressive oxidation of the Ti layer through electromigration of oxygen ions from the underlying PCMO is strictly correlated to the electroforming protocol and to the device resistance state, thus demonstrating that the Ti/PCMO junction, and in particular the TiO\(_x\) layer, plays a crucial role for the resistive switching behaviour of these devices.

![Fig. 1. Summary of HAXPES core level spectra for the as-prepared (“pristine”) and electroformed states #1 - #3 correspondent to increasing device resistance: (a) Ti 2p spectra for the Ti top electrode; (b) lineshape comparison of the Ti 2p spectra to show the relative variation of the Ti\(^0\) (metallic) vs. the Ti\(^{4+}\) (oxide) terms; (c) Mn 2p spectra for the region of the underlying PCMO layer close to the boundary with the Ti film.](image)

References