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Doctoral Dissertation  
Doctoral Program in Physics (33<sup>rd</sup> cycle)

# **Resistive switching devices with improved control of oxygen vacancies dynamics**

## **Summary**

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According to some analysts, the information revolution responsible for the unprecedentedly fast technological development of last decades is about to give way to the “Neuromorphic Revolution”, led by big data and artificial intelligence. Similar forecasts are made possible by the huge Research efforts that have been providing us deeper knowledge and enhanced control of emerging technologies expected to be the basis for next-generation computing. In this framework, resistive switching is one of the most relevant phenomena, and resistive switching devices are among the leading players in the upcoming breakthrough of neuromorphic computing. However, some open questions and unresolved issues have yet to be faced. Primarily, device reliability and integration with current technology standards need to be improved. In this Thesis, such aspects are accounted for through the investigation of possible strategies to deal with these issues in well-defined cases. Particularly, a specific class of resistive switching devices is investigated, focusing on the valence change memory (VCM) effect. This mechanism relies on the drift of oxygen anions, under the effect of an external voltage, within a metal oxide that consequently undergoes variations of its electrical resistance. Investigation of different oxides and different structures is reported, proposing possible technological strategies to tailor the device performances through an enhanced control on the key aspect in the VCM mechanism, namely the oxygen vacancies dynamics. The first resistive switching material investigated is zinc oxide. Characterized by a wide direct band gap, a large exciton energy, a good thermal and chemical stability, as well as biocompatibility, ZnO is widely employed for applications ranging from electronics to medicine. Such a versatility comes from the richness of nanostructures it can provide. In the field of resistive switching, zinc oxide is typically employed in form of thin films or nanowires, and in this Thesis the effect of a complementary action of these structures is reported, showing the improvements achieved in terms performances with respect to Pt/ZnO-film/Pt devices. The resistive switching instability observed for these latter, explained by a lack of ionic species needed for the redox reactions of VCM mechanism, is mitigated by hydrothermally grown ZnO nanowire arrays. The additional zinc oxide layer represented by the nanowires turns out to be affected by a slight understoichiometry suitable to supply the underlying ZnO film with a surplus of oxygen vacancies, thus filling the lack of ionic species for VCM resistive switching. Acting as an oxygen vacancies reservoir, zinc oxide nanowires provides significant performance improvements, with endurance and retention results outperforming previous data reported in literature for similar devices. Following the study on ZnO, investigations on hafnium dioxide are presented. Widely employed in electronics as a high-k dielectric, HfO<sub>2</sub> naturally emerged among the possible metal oxides to be exploited for resistive switching devices thanks to the well-established technological knowledge of its properties.

In this Thesis, the case of resistive memory cells employing tungsten as oxidizing electrode for VCM-based devices is discussed. The  $\text{HfO}_2/\text{W}$  interface has been indeed previously reported to be affected by critical resistive switching instabilities hindering them from providing reliable performances, and the insertion of a titanium buffer layer between hafnium dioxide and tungsten has been proposed to mitigate such issue. An extensive investigation of this stabilization strategy is presented, with systematic electrical characterizations on more than one hundred devices. The role played by titanium is analysed at different stages of resistive switching operations varying both thickness and composition of the buffer layers: in addition to pure-Ti films with thickness of 1 nm, 3 nm and 5 nm, a mixed W-Ti layer, with 10% in weight of titanium and thickness of 3 nm, is employed. The impact of the buffer layer properties on the main resistive switching parameters, namely the forming voltage ( $V_{\text{FORMING}}$ ), the switching voltages ( $V_{\text{SET}}$  and  $V_{\text{RESET}}$ ) and the resistance levels ( $R_{\text{LRS}}$  and  $R_{\text{HRS}}$ ), is reported and discussed. Investigation of the forming process by means of conductive atomic force microscopy (C-AFM) is also presented, showing the filamentary nature of the observed resistive switching. Finally, results from tests in the dynamic operational regime are reported, showing how the different oxidizing activity of titanium and tungsten play a key role in the involved VCM mechanism. Thanks to a more efficient oxygen extraction, Ti can indeed hinder the more energy demanding tungsten oxidation, especially avoiding the metastable oxides formed before  $\text{WO}_3$  is achieved and thus mitigating, or avoiding, resistive switching instabilities.