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Non-volatile resistive switching in the Mott insulator (V_{1-x}Cr_x)₂O₃

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Abstract

The discovery of non-volatile resistive switching in Mott insulators related to an electric-field-induced insulator to metal transition (IMT) has paved the way for their use in a new type of non-volatile memories, the Mott memories. While most of the previous studies were dedicated to uncover the resistive switching mechanism and explore the memory potential of chalcogenide Mott insulators, we present here a comprehensive study of resistive switching in the canonical oxide Mott insulator $(V_{1-x}Cr_x)_2O_3$. Our work demonstrates that this compound undergoes a non-volatile resistive switching under electric field. This resistive switching is induced by a Mott transition at the local scale which creates metallic domains closely related to existing phases of the temperature-pressure phase diagram of $(V_{1-x}Cr_x)_2O_3$. Our work demonstrates also reversible resistive switching in $(V_{1-x}Cr_x)_2O_3$ crystals and thin film devices. Preliminary performances obtained on 880 nm thick layers with 500 nm electrodes show the strong potential of Mott memories based on the Mott insulator $(V_{1-x}Cr_x)_2O_3$.

Keywords: Mott insulators, V₂O₃, Mott transition, resistive switching, non-volatile memory, ReRAM.

1. Introduction

Resistive Random Access Memories (ReRAM) are considered as one of the most promising technologies for future non-volatile memories. They are based on resistive switching mainly related to two physical mechanisms: ionic electromigration (anionic for OxRAM and cationic for CBRAM) and thermochemical reactions (typically in NiO) [1, 2, 3]. But recently the insulator to metal transition (IMT) in Mott insulators has focused much attention due to its serious potential as an alternative mechanism for ReRAM [4]. Mott insulating state can be usually destabilized by pressure and doping into a correlated metal phase via an isostructural electronic phase transition, as shown for example in the temperature-pressure phase diagram of V_2O_3 in Fig. 1(a) [5]. However recent works [4, 6, 7, 8] have shown that electric field can also destabilize the Mott insulating state and trigger a non-volatile resistive switching in these materials. Studies performed on the chalcogenide compounds AM_4Q_8 (A=Ga, Ge; M=Nb, V, Ta; Q=S, Se) have demonstrated that this resistive switching (RS) originates from an avalanche breakdown phenomenon [7] which causes the collapse of the paramagnetic Mott insulator state at the nanoscale [10] and results in the creation of granular conductive filaments [11].

This discovery on the chalcogenide AM_4Q_8 compounds raises the question of the universal nature of this new type of non-volatile resistive switching. We have therefore sought such resistive switching in the most famous canonical narrow gap Mott insulator, namely $(V_{1-x}Cr_x)_2O_3$. We report here that this oxide Mott insulator exhibits a non-volatile resistive switching of the same physical nature as the AM_4Q_8 compounds. Moreover we show that the performances of a $(V_{1-x}Cr_x)_2O_3$ memory cell obtained on a device mostly compatible with microelectronics standards are very promising.

2. Material and methods

2.1. $(V_{1-x}Cr_x)_2O_3$ crystals synthesis

 V_2O_5 (Aldrich, > 99.6 %) powder was first dried at 400°C, then mixed with Cr_2O_3 (Prolabo, 99.9 %) in the 97.5 : 2.5 molar ratio, and then heat-treated at 900°C for 10h under a 95% Ar – 5% H₂ gas flow. Half a gram of the obtained ($V_{0.975}Cr_{0.025}$)₂O₃ powder was then placed in a silica tube together with 40 mg of sulfur as a vapor phase transport agent. The tube was vacuum sealed, heated up to 1050°C in a temperature gradient (\approx 10°C/cm) furnace and then cooled down at -2°C/h to 900°C, before a faster cooling (-300°C/h) to room temperature. Energy Dispersive X-ray Spectroscopy analyses carried out on the obtained crystals (typical size 100 × 50 × 300 µm) indicate that the V / Cr ratio is close to the nominal value and show the absence of sulfur impurities in the crystals.

2.2. Thin film synthesis and device preparation

Thin films of $(V_{0.95}Cr_{0.05})_2O_3$ were deposited by reactive co-sputtering of V and Cr targets in Ar/O₂ discharge [12], leading to thicknesses in the 100-880 nm range. Post deposition annealing at 500°C in a reducing atmosphere yields crystallized and single-phased $(V_{0.95}Cr_{0.05})_2O_3$ layers as checked by X-Ray diffraction (XRD). In V₂O₃, deviation from the ideal V/O ratio by 1.75 % lowers the magnetic ordering temperature (paramagnetic metal PM to antiferromagnetic insulator AFI transition, see Fig. 1(a)) from 155 K to 11 K [13]. But our $(V_{0.95}Cr_{0.05})_2O_3$ thin films deposited on SiO₂/Si substrates and measured with four probes in a planar configuration exhibit a paramagnetic Mott insulator PMI – AFI transition temperature (158 K) very close to the expected one (175K), which indicates that they are almost stoichiometric. This prevents spurious electromigration processes associated to ionic diffusion and excludes potential OxRAM/CBRAM mechanisms. Devices based on a symetric TiN / $(V_{0.95}Cr_{0.05})_2O_3$ / TiN MIM structure were subsequently realized with via diameters in the 330 - 1600 nm range.

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