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Magnetism as a probe of the origin of memristive switching in *p*-type antiferromagnetic NiO

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We induced bipolar resistive switching in *p*-type nickel oxide. By probing the magnetic properties of the films, we proved that bipolar resistive switching in this antiferromagnetic oxide was due to the formation and rupture of oxygen-vacancy filaments, rather than electrochemical growth and dissolution of nickel-ion filaments. In the low resistive state, oxygen-mediated super-exchange interaction was suppressed along the conductive paths. This led to a reduction of the saturation moment but not the appearance of a ferromagnetic phase, excluding the formation of nickel filaments. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4834795]

Amongst all the technologies considered as promising alternatives to silicon for non-volatile, high-capacitance mass storage, electric-field-induced resistive switching in oxide semiconductors has attracted much interest due to its low cost and easy integration with the complementary metal-oxide semiconductor (CMOS) technology.[1] A wide variety of oxides have been reported to show resistive switching but the physical mechanism has not yet been fully understood. The switching event is a complicated electronic and ionic process, which may involve more than one mechanism, including charge trapping within the energy gap,[2–7] change of the order parameters in ferroelectric[8] or ferromagnetic[9] oxides, reduction of valence states in mixed-valence oxides,[10,11] uniform migration of oxygen vacancies within the depletion layer of Schottky contacts,[12,13] or the formation and rupture of conductive filaments across oxide insulators.[14–24]

At the current stage, the industry is mainly focusing on systems in which filamentary conduction is the dominant mechanism.[15,16] This is because highly reliable switching can be obtained in low-cost metal-insulator-metal structures where the insulator is a commonly used binary oxide such as TiO_2,[14,15] Ta_2O_5,[16] ZnO,[17] SiO_2,[18] and NiO.[19–22] While experimental evidences convincingly prove[23,24] that conductive channels are formed and broken under the application of a bipolar electric field, an outstanding question that remains to be addressed is whether these channels consist of oxygen-vacancy filaments or metal-ion filaments. An answer to this question cannot be given based on electrical characterization of the system, because both types of channels have similar conductivities. Advanced microscopy investigations proved challenging because of the nano-size of the channels and the heavy dependence of the results on specimen preparation techniques. Unambiguous discrimination is possible if the formation of either types of channel leads to a macroscopic change of non-electrical properties, for instance, magnetic properties. In this respect, *p*-NiO provides a unique test-bed since it is a well-known antiferromagnetic insulator and shows filamentary-type switching.

We have induced bipolar resistive switching in *p*-type antiferromagnetic NiO. The system shows long retention time in both resistive states and a resistance that does not sensibly change with device size, which are typical features of filamentary-type switching. The overall magnetic moment of the film was found to be smaller in the low resistive state (LRS) and no remanence was observed in the high resistive state (HRS). From our analysis of the magnetic properties of the film in the two resistive states, we conclude that the conductive channels consist of oxygen-vacancy filaments rather than Ni-ion filaments.

The studied system consists of a 100 nm-thick nickel oxide (NiO) film sandwiched between a highly polished, atomically flat 0.7% Nb-doped strontium titanate ⟨100⟩ substrate (NSTO, used as the bottom metallic electrode) and a platinum (Pt) top electrode. The bilayer NiO/Pt was grown on the NSTO substrate at room temperature in high vacuum by pulsed laser deposition (PLD). A preliminary investigation of the structural properties of the NiO films showed that the films were polycrystalline with an averaged grain size of 250 nm and a surface roughness of less than 2 nm (see Fig. 1).
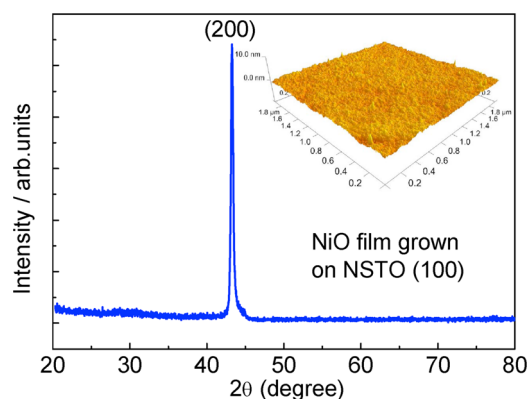

FIG. 1. X-ray diffraction pattern of NiO film grown on NSTO with crystal phase (100). Inset shows the typical AFM scan of the film.

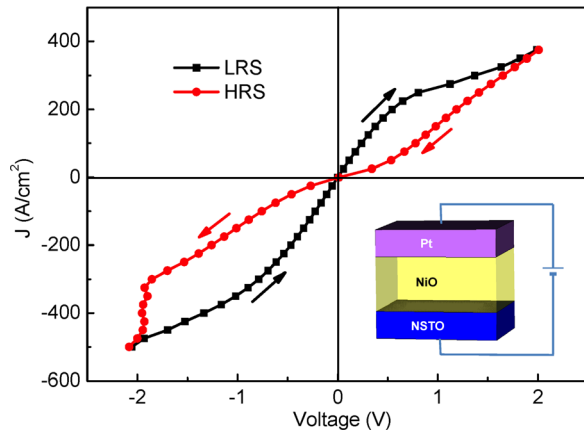a)Electronic mail: aruotolo@cityu.edu.hk

FIG. 2. Bipolar d.c. current-voltage switching operation of the devices with LRS (black line) and HRS (red line). Inset shows the schematic representation of the studied system.

FIG. 4. Area-dependent resistance in the two states.

The NiO films showed p-type conduction with carrier concentration $N \sim 10^{18}$ cm^{-3}, as detected by measuring the four-point sheet resistance in magnetic field up to 1 T with a commercial Hall measurement system. p-type conductivity in NiO is well known to be due to Ni-vacancies.[25]

Micro-devices were fabricated through three photolithographic steps and lift-off patterning. Before the deposition of the bilayer, windows were opened in the spun photoresist, and the device regions were defined by lift-off. Through alignment of a second lithography mask, the square junctions were isolated and planarized by the deposition of SiO$_2$. Finally, a 200 nm-thick Pt counter-electrode was defined for each junction. We fabricated junctions with dimensions ranging from 16×16 μm^2 to 200×200 μm^2 that could be independently biased.

Electrical characterization of the devices was carried out by using standard laboratory electronics. Fig. 2 shows the typical J–V characteristic of our devices. The resistance of the film could be switched between two stable states, namely, LRS and HRS. The hysteresis was stable over repeated sweeps. This behavior is in agreement with that reported by other authors[19,20] in similar devices employing NiO.

Switching could be achieved by either scanning the hysteretic J–V or by applying short ($t_p = 1$ μs in Fig. 3) voltage
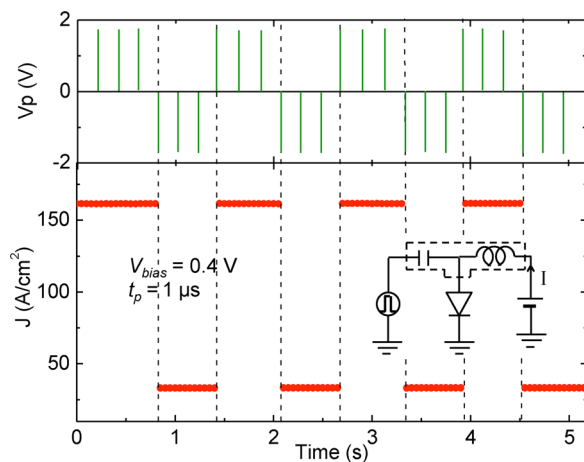
pulses. In the pulsed working mode of Fig. 3, the switching was detected by reading the current at a fixed voltage $V_{bias} = 0.4$ V, which is smaller than the threshold voltage (2 V). A standard bias tee was used to supply simultaneously the pulses and the bias voltage to the junction. The resistive switching ratio was same as that evaluated from the hysteretic J–V curve, at the same bias.

The system shows all the typical features of filamentary-type switching.[24] In filamentary-type switching, the resistance of the device at a fixed bias current does not sensibly depend on the device size because the nano-filamentary channels behave as shorts.[20,23] This is in agreement with our observation (see Fig. 4). In order to further exclude interface-type switching, which is due to trapping of charge near the electrodes,[2–7] we measured the read endurance and the retention in our devices. While read endurance under short repeated pulses is usually stable in both interface- and filamentary-type switching, retention time measured under continuous flow of current is stable only for filamentary-type switching.[7] In Fig. 5, we show the voltage measured across the same device of Fig. 2 under continuous bias current of $J = 125$ A/cm^2, after setting the device in either resistive states. The long retention time excludes an interface-type effect.

While it is commonly accepted that filamentary switching is due to the formation and rupture of conductive

FIG. 3. Bipolar switching induced by voltage pulses with a duration of $t_p = 1$ μs. Inset shows the measurement setup.
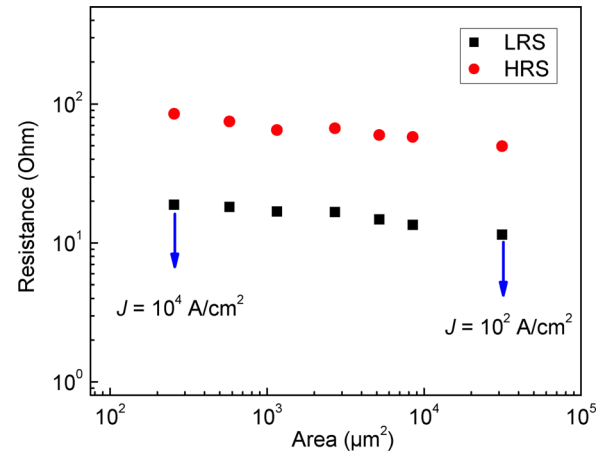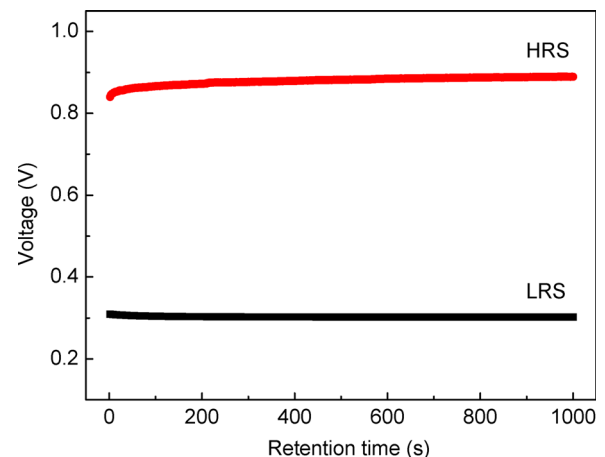

FIG. 5. Retention time of both states under continuous bias current.

nano-channels across the oxide film,[23,24] it is less clear whether the filaments consist of clustered vacancies or metal-ions. An unambiguous answer to this question can come from the study of the magnetic properties of the oxide films in the two resistive states. We measured the magnetization loop of a large device with area $A = 3\,mm^2$ and same thickness of NiO (100 nm) in the two states at low temperature (Fig. 6). The loop was first measured when the sample was in the LRS. The film showed a typical antiferromagnetic magnetization loop with negligible remanence. Subsequently, the sample was set in the HRS, then disconnected from the electric circuit, mounted again in the magnetometer, and the magnetization loop was measured again. An increase of the magnetic moment by more than 30% was observed. Despite this large change of magnetic moment, we could not appreciate any change of remanence in the film, which excludes the formation of a ferromagnetic phase. The experiment was repeated several times.

Stoichiometric NiO is an almost-insulator with a band-gap of $\sim 4\,eV$.[25] The top of the valence band is formed by oxygen $2p$ states, while the bottom of the conduction band is Ni-$3d$ like. Electrical conductivity in NiO can be due to both nickel vacancies (V_{Ni}) or oxygen vacancies (V_O). V_{Ni}'s are double acceptors and introduce shallow levels in the band-gap, whereas V_O's are double donors and introduce deep localized states. Under typical growth conditions, NiO is deficient with Ni^{2+} cations, and therefore shows p-type conductivity. NiO crystallizes with NaCl-type structure, with ferromagnetic (111) Ni layers antiferromagnetically coupled along the [111] direction. In the (111) Ni layers, ferromagnetic interaction is partially compensated by oxygen-mediated antiferromagnetic interaction. This results in a net ferromagnetic exchange interaction $J_F \sim 1\,eV$ (Ref. 26), and therefore a weak net magnetic moment that lies along the (111) plane. A strong Ni-O-Ni antiferromagnetic super-exchange interaction $J_{AF} \sim 20\,eV$ (Ref. 26) is established along the [111] direction and determines the antiferromagnetic nature of the material.

While both V_{Ni} and V_O reduce the overall magnetic moment and increase the conductivity,[27] the effect of

clustering of vacancies or metal-ions has different effects on the magnetic properties of the film. A clustering of Ni-ions, possibly organized in nano-filaments, would lead to a significant increase of J_F. As a result, a non-negligible remanence and coercivity should appear in the magnetization loop. Our measurements therefore excluded electrochemical growth of Ni-ion filaments during the switching process. It should also be noted that the growth of Ni-ion filaments would result in a strong, non-uniform distribution of V_{Ni}'s. Clustering of V_{Ni}'s was demonstrated[27] to lead to half-metallic properties, and therefore, once again, to the appearance of a ferromagnetic phase. Besides, it has recently been experimentally demonstrated,[28] by using magnetic force microscopy, that V_{Ni}'s are sources of ferromagnetism with high coercivity.

The results shown in Fig. 6 can only be explained by admitting the clustering of oxygen vacancies organized in filaments. n-type conductivity along these channels is increased while oxygen-mediated antiferromagnetic coupling is suppressed. This leads to a local reduction of J_{AF}, detected as an overall reduction of the magnetic moment, that is not accompanied by an increase of J_F, and therefore no magnetic phase is detected.

Other authors[29] have observed exchange bias in Pt/NiO/Pt capacitors under unipolar switching and therefore concluded that the memristive switching was due to the formation of Ni-filaments across the film. In the upper-left inset in Fig. 6, we show the magnetization loop measured at $T = 10\,K$ in perpendicular field, measured after setting the sample in the LRS. A magnetic field of 1 T was applied during cooling along the same direction. We did not observe any significant increase of remanence or a shift of the loop along the field axis. This might suggest that the origin of unipolar switching observed in some binary oxides is different from the case of bipolar switching. Therefore, we limit our conclusions to the case of bipolar switching, which is the case of interest for practical applications.

In conclusion, we induced bipolar resistive memory switching in p-type antiferromagnetic NiO grown on Nb-doped STO. The electrical characterization of patterned devices of different sizes indicated clearly that the effect is due to formation/rupture of conductive nano-filaments in the NiO. By measuring the magnetic properties of the system in the two resistive states, we can exclude that switching is due to the formation of Ni-ion filaments across the device. We have demonstrated that the switching is due to the formation and rupture of oxygen-vacancy filaments. Our results are relevant to other similar systems.
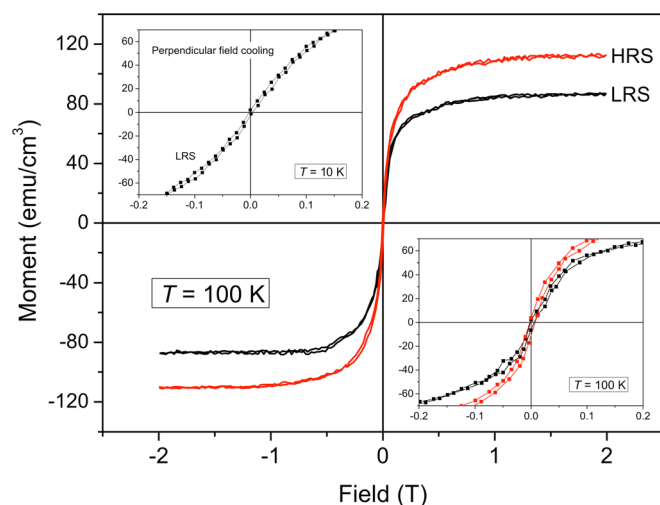

FIG. 6. Magnetization versus in-plane applied field of a 100 nm-thick film at $T = 100\,K$ with LRS (black line) and HRS (red line). The bottom-right inset shows an enlargement of the same loop. The upper-left inset shows the field-cooling magnetization loop in perpendicular applied field at $T = 10\,K$.

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