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Non-volatile, reversible switching of the magnetic moment in Mn-doped ZnO films

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We report on the observation of a non-volatile, reversible switching of the magnetic moment in Mn-doped ZnO thin films. The system is a typical oxide memristor based on an oxygen-deficient semiconductor oxide. In the present study, the oxide semiconductor is ferromagnetic at room temperature. We found that the bistable switching of the resistive state was accompanied by a bistable switching of the magnetic moment at room temperature. Our results support the hypothesis that ferromagnetism in Mn-doped ZnO is mediated by oxygen-vacancies. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4793639]

I. INTRODUCTION

Amongst the oxide semiconductors, the II-VI compound zinc oxide (ZnO) is considered the most interesting because of its unique combination of electrical, optical, piezoelectric, and acoustic properties. Moreover, ZnO can be doped with transition metals to induce ferromagnetism at room temperature, which makes it a promising semiconductor for application in spintronics. Ferromagnetism at room temperature can be induced in ZnO by doping with low concentrations of manganese (Mn). The magnetic moment in this compound depends, in a non-trivial way, on both the concentration of Mn and the concentration of the oxygen vacancies. Theoretical studies[1] have predicted that the origin of the magnetic moment must be ascribed to exchange interaction between Mn cations mediated by oxygen vacancies. This prediction has recently been confirmed by our group.[2]

An electrically induced change of concentration of oxygen vacancies in oxide semiconductors[3,4] is at the origin of the memristive effect that has recently attracted great attention for its potential for application in non-volatile memories. It is reasonable to expect that, if memristive devices are fabricated by using Mn-ZnO, the reversible electrical phase transition in the oxide must correspond to a reversible change of the magnetic properties. This would represent an original and further confirmation that ferromagnetism in Mn-ZnO is mediated by oxygen vacancies.

We induced memristive switching in 4%-Mn-doped ZnO films and found that the bipolar resistive switching is accompanied by a switching of the magnetic moment in the film at room temperature. The switching of the magnetic moment is reversible and not volatile.

II. EXPERIMENT

The 4%-Mn-doped ZnO films were grown by pulsed laser deposition (PLD). A pulsed KrF excimer laser ($\lambda = 248$ nm) was used with a repetition rate of 10 Hz. The films were grown at room temperature and in low oxygen pressure of 0.4 mbar in order to obtain highly oxygen-deficient films.[2] In Fig. 1, we show the typical X-ray diffraction pattern of the grown films. Only the diffraction peaks (002) and (004) from the ZnO wurtzite structure could be detected, thus excluding the presence of Mn_xO_y secondary phases. By using the Debye-Scherrer formula, we could estimate a crystal grain size larger than 300 nm. The films showed n-type conduction, as detected by measuring the four-point sheet resistance in magnetic field with a commercial Hall measurement system. A carrier concentration of $N \sim 10^{12}$ cm^{-3} was measured. Photoluminescence (PL) spectra were measured in order to exclude a significant presence of Zn vacancies or Zn interstitials as potential donors. Energy dispersive spectroscopy (EDS) was used to exclude contamination of unintentional dopants, like gallium, aluminum, and indium.

In order to induce resistive switching, films were grown on atomically flat, Nb-doped strontium titanate (Nb-STO)
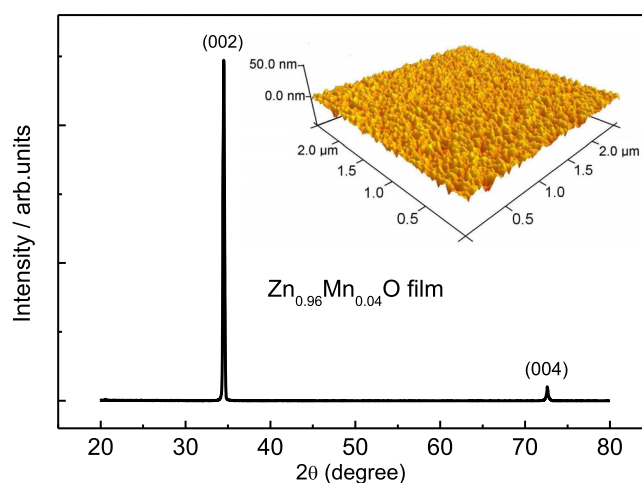

FIG. 1. X-ray diffraction pattern of a $Zn_{0.96}Mn_{0.04}O$ film. Inset shows the typical AFM scan of films.

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substrates. The substrate was used as a bottom metallic electrode, while a top platinum (Pt) counter-electrode was deposited without breaking vacuum.

While the substrate (and therefore the bottom Nb-STO/Mn-ZnO interface) was atomically flat, atomic force microscope measurements showed that the roughness at the top surface of the Mn-ZnO film (and therefore the roughness of the Mn-ZnO top interface) was ~2 nm. As will be shown later, this favors the formation of a Schottky barrier at the bottom interface and an ohmic contact at the top interface.

Current density-voltage (J–V) characteristics were recorded at room temperature by using standard laboratory electronic instrumentation. The devices were biased in current, as always is for memory cells. In the following, positive current corresponds to forward bias of the Schottky interface, i.e., current flowing from the bottom Nb-STO to the top Pt electrode.

Magnetization measurements were carried out by a commercial vibrating sample magnetometer. The shown hysteresis loops were extracted from those recorded by subtracting the measured linear contribution of the substrate.

III. RESULTS AND DISCUSSION

Fig. 2 shows the typical J–V characteristic of our film devices with a Mn-ZnO film thickness of 120 nm. The as-grown samples (Fig. 2 inset) showed a rectifying J–V curve, the polarity of which revealed that the electrical behavior was dominated by the Schottky-like interface at the bottom Nb-STO/Mn-ZnO interface, whereas the top interface is ohmic, in agreement with the AFM measurements. A single irreversible forming step was necessary before the devices exhibited hysteretic J–V. The forming step occurred at ~10 V in reverse bias.

After the forming step, the devices could be switched between two stable states. When a reverse threshold current is reached, the system switches in a low resistive state (LRS), whereas when a forward threshold current is reached the system switches in a high resistive state (HRS). The

hysteresis in the J–V characteristic is stable over repeated sweeps. Once the system is set in either state, the state is stable under repeated reading cycles, as shown in Fig. 3. It must be noticed that the applied reading pulses have a duration of 0.5 s. This long pulse duration is responsible for the loss of retention in the LRS.

Bipolar switching in Mn-doped ZnO is known[5] to be a non-filamentary, interface type switching. According to the non-filamentary model for electro-resistive switching in Schottky diodes,[6–10] during the forming process, when a negative threshold electric field is reached, carriers have enough energy to ionize some of the valence bonds of the lattice. During bipolar switching, the negative electric field on the space charge region of the Schottky junction exerts its force on the negative O ions in such a way as to displace them far from the interface. This corresponds to an accumulation of oxygen vacancies under the interface. Oxygen vacancies are double-donor dopants, which favor electron tunneling through the Schottky barrier, therefore, the system switches in the LRS. It must be understood[11] that, when the external reverse voltage is brought back to zero, the negative built-in electric field acts against the oxygen gradient force, hence inhibiting the diffusion of O ions in the opposite direction until a positive electric field is reached, which activates the opposite process and favors quasi-uniform distribution of the oxygen over the film thickness.

If the oxygen vacancy distribution is different in the two resistive states and ferromagnetic exchange in Mn-ZnO is mediated by oxygen-vacancy, a change of resistance should correspond to a change of magnetic moment in the film. We measured the magnetization loop of the film device in the two states at room temperature (Fig. 4). The loop was first measured when the sample was in the LRS. Subsequently, the sample was set in the HRS. The device was disconnected from the electric circuit, mounted again in the magnetometer, and the magnetization loop was measured again. We found an increase of the magnetic moment by 40% in samples with a thickness of Mn-ZnO of 120 nm. In order to verify the reversibility of the magnetic switching, the sample
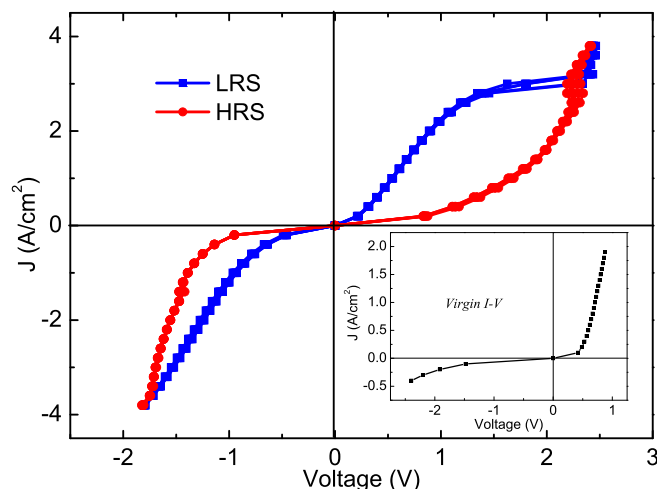

FIG. 2. Bipolar dc current-voltage switching operation of a 120 nm-thick, 2×2.5 mm^2-wide film device. Inset shows the current-voltage characteristic before the forming process.
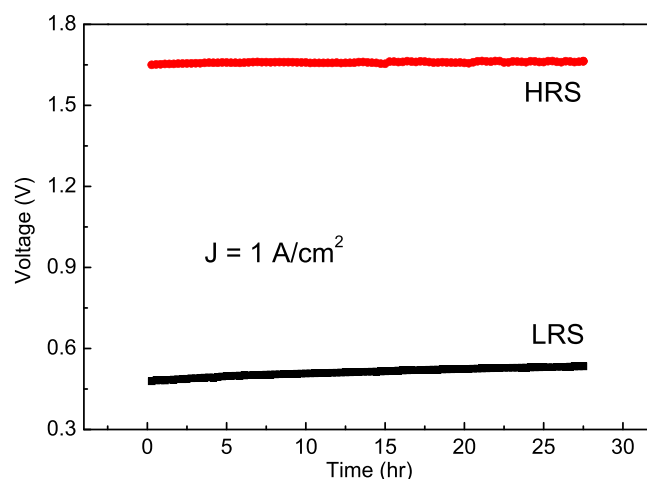

FIG. 3. Read cycle in both states over repeated read operations of a 120 nm-thick, 2×2.5 mm^2-wide film device. A current pulse of $J = 1$ A/cm^2 and duration 0.5 s are applied during reading with a repetition rate of 60 s.
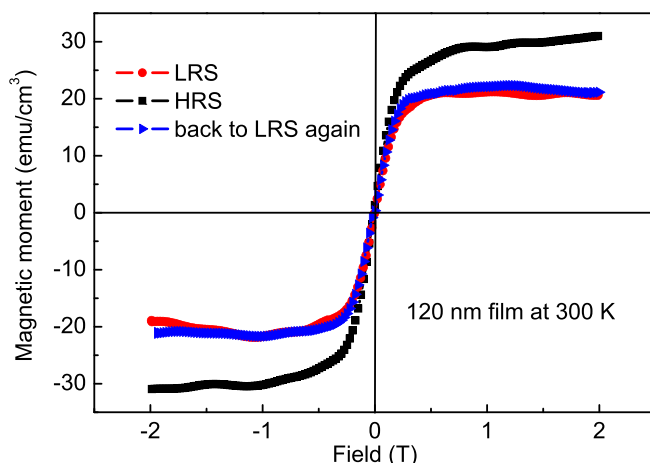
FIG. 4. Magnetization versus in-plane applied field of a 120 nm-thick, 2×2.5 mm^2-wide film device at T = 300 K. The change of magnetic moment at saturation ΔM_S is 40%.

was connected again to the electrical circuit to reset it in the LRS. Indeed, the original magnetic moment could be recovered. A reversible switching of the resistive phase corresponds to a reversible switch of the magnetic phase.

When the system is in the LRS, the oxygen vacancies are accumulated under the Nb-STO/Mn-ZnO interface and trapped in the space charge of the Schottky junction. This means the rest of the film is depleted of oxygen vacancies and the overall magnetic moment is smaller. In the HRS, the oxygen vacancies are uniformly distributed along the film thickness and the magnetic moment is increased. This behavior is in agreement with the hypothesis that ferromagnetism in Mn-ZnO is mediated by oxygen vacancies. A change of the distribution of oxygen vacancies results in a change of the magnetic moment in the film.

It must be noticed that coercivity and remanence of Mn-ZnO are always very small and, therefore, hard to estimate in very thin films. This hinders us from making a comparison between the values of these parameters in the two states,

leaving the magnetic moment as the only reliable parameter to describe the magnetic phase.

IV. CONCLUSIONS

We have induced bipolar resistive memory switching in Schottky contacts to Mn-doped ZnO films. We found that the switching of the resistive state is accompanied by a switching of the magnetic moment. This represents a new experimental confirmation that ferromagnetism in this compound is mediated by oxygen vacancies.

ACKNOWLEDGMENTS

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