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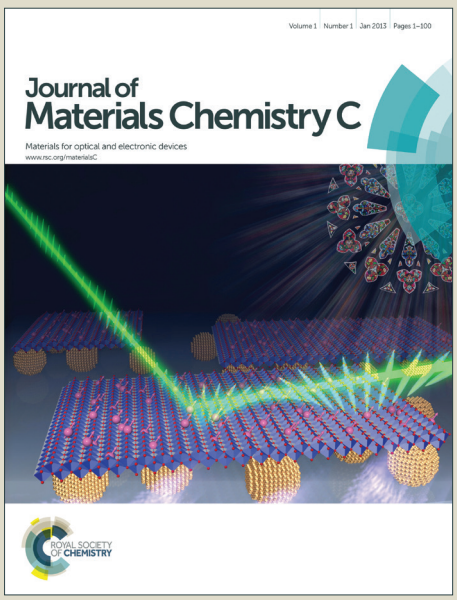





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ARTICLE

# Electric Field Control of Magnetism in Ti/ZnO/Pt and Ti/ZnO/SRO Devices

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We report electric field induced magnetic switching behaviours in un-doped ZnO films grown on Pt and $SrRuO_3$ (SRO) bottom electrodes. The coexistence of great resistive and magnetic switching was observed in both devices under an applied electric field, but the magnetic change is opposite in ZnO films grown on Pt and on SRO electrodes. By fitting the current-voltage curves of the samples, we found that we could attribute the resistive switching behavior to filamentary conduction in the Ti/ZnO/Pt device and interfacial Schottky barrier effects in the Ti/ZnO/SRO device. The underlying mechanism for magnetic switching behavior in Ti/ZnO/Pt and Ti/ZnO/SRO devices is discussed based on their resistive switching mechanism. Our work suggests that the magnetic properties of un-doped ZnO films can be greatly altered by applying a small voltage.

## Introduction

The rapid development of spintronics requires materials with both semiconducting and magnetic properties at room temperature.[1] ZnO-based dilute magnetic oxide semiconductors, are promising candidates for such spintronics materials, and have attracted intense research interest.[2-5] Control of room temperature ferromagnetism (FM) using an electric field is a key issue for the future development of low power spintronics.[6,7] Recently, magnetic switching behaviours in transition-metal doped ZnO films controlled by a low voltage during resistive switching (RS) has been reported by several research groups.[8-10] It is known that the FM in transition-metal doped ZnO films could be affected by the extrinsic factors such as dopant clustering, impurity magnetic phases, etc, which are difficult to detect when the impurity clusters are quite small. The effect of dopant element could not be ruled out in these transition-metal doped films. Here we report magnetic switching behaviors in un-doped ZnO films grown on Pt and $SrRuO_3$ (SRO) bottom electrodes (BEs). In both cases, the ZnO films were deposited under the same conditions. A large magnetic change was observed in both devices under an applied electric field, suggesting that the electric field induced magnetic switching behaviors are intrinsic properties of the films. It is found that the magnetic variation is just opposite in ZnO films grown on Pt and SRO BEs. The underlying mechanism is discussed in this letter.

## Experimental

A schematic of the device layout is shown in Fig.1 (a). For the Ti/ZnO/SRO device, an SRO layer of about 120nm was deposited as BE on a commercially available (001) $LaAlO_3$ (LAO) crystal substrate using a pulsed laser deposition (PLD, KrF, λ=248 nm) technique. Then ZnO films of approximately 70 nm were grown on the SRO/LAO under a low oxygen pressure of 3.8mTorr at 400℃ with the intention of producing abundant oxygen vacancies ($V_O$s). For the Ti/ZnO/Pt device, ZnO films with the same thickness were grown on commercial Pt/Ti/$SiO_2$/Si substrate under the same preparation conditions. In order to measure the electrical and magnetic properties, Ti top electrodes (TE) with a diameter of 200μm, covering approximately 10.6% of the film area, were deposited on the ZnO films by sputtering through a shadow mask.

The crystal structure of the as-deposited ZnO films was investigated using X-ray diffraction (XRD, X'pert PRO MPD) with Cu Kα radiation (λ = 0.15406 nm). Atomic force microscopy (AFM) images were acquired using a Veeco Nanoscope IV scanning probe microscope operated in tapping mode. Current-voltage (*I–V*) characteristics were measured at room temperature using a semiconductor characteristic system (Keithley 2612A). During the measurements, the sweep voltage was applied to the Ti TE in the sequence 0→positive→0→negative→0 while the SRO or Pt BEs was grounded, as shown in Fig.1 (a). A positive bias was defined such that current flowed from the TE to BE. Magnetic measurements were carried out using a physical property measurement system (PPMS-6700) and a superconducting quantum interference device (SQUID), with the magnetic field applied parallel to the film plane. The diamagnetic contributions of the substrates were all extracted. Notably, Teflon tweezers were used to handle all the samples so as to eliminate possible contamination of the samples during the whole process.

## Results and discussion

The XRD patterns of typical ZnO films deposited on Pt and SRO BEs are shown in Fig.1 (b). It can be seen that in addition to the diffraction peaks from the substrates, only the (002) peak from the ZnO wurtzite structure was detected within the XRD detection limit. This indicates that the as-deposited ZnO films on both the Pt and SRO BEs have a strongly oriented c-axis, which is in agreement with a previous report.[11] The AFM image showed that the root-mean-square values of the surface roughness of the films deposited on Pt and SRO were 3.545nm and 3.687nm, respectively, as shown in Fig.2 (a) and Fig.2 (b).

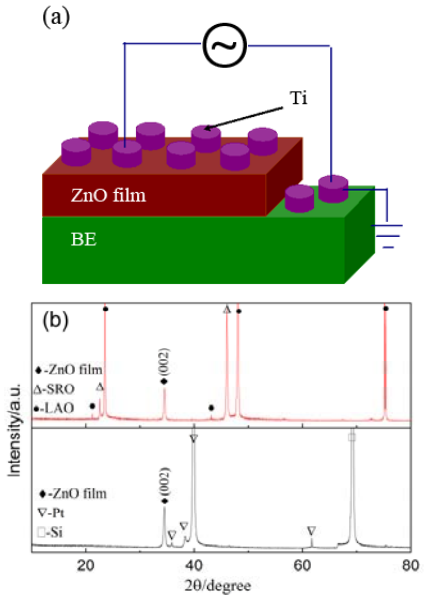


Fig.1 (a) A schematic structure of the Ti/ZnO/BE devices, (b) XRD patterns of typical ZnO films deposited on Pt and SRO BEs.

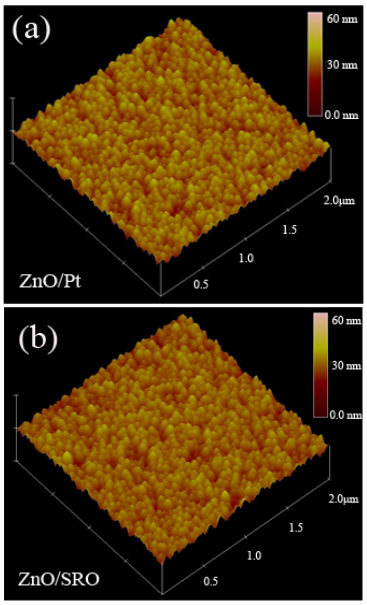


Fig.2 Typical AFM images of ZnO films deposited on Pt (a) and SRO (b) BEs

Fig.3 shows representative *I-V* characteristics of the ZnO films with Pt and SRO BEs. It may be seen that the ZnO films show different RS patterns despite having the same crystal orientation and similar film microstructures. RS behaviour is usually attributed to two different mechanisms: filamentary conduction and interfacial effects.[12] The former stems from the formation and rupture of Vo-based conductive filaments in the bulk of oxide material, whereas the latter occurs at the interface between the dielectric oxides and the metal electrodes. It can be seen that the ZnO film with the Pt BE shows a bipolar RS with a sudden current jump at $V_{SET}$ = 0.82V and $V_{RESET}$ = -1.20V(see Fig.3 (a)), suggesting the formation and rupture of Vo-based conductive filaments in the ZnO matrix.[13,14] The *I-V* curve for the ZnO film with the Pt BE is plotted on a double logarithmic scale in the right-bottom inset in Fig.3 (a)). Obviously, the LRS shows Ohmic behaviour with a slope close to 1, which confirms that the conduction mechanism in the LRS conforms to the local filamentary mode.[15]

In contrast, the RS behaviour of the ZnO film with SRO BE has smoother resistive transitions without any abrupt change in the *I-V* curve, as shown in Fig.3 (b). This suggests that the mechanism is based an interface effects. The asymmetric *I-V* curve in the HRS may indicate the formation of a Schottky-like barrier at the ZnO/SRO interface. This is confirmed by the linear ln$I$-$V^{1/2}$ plot, which is a typical behaviour of the Schottky barrier mechanism in the HRS[16] (see right-bottom inset in Fig.3(b)).

In addition, the retention properties, that is, the ability of the resistance to remain in the HRS or LRS for a long period of time after removing the applied electric field on the device, of the Ti/ZnO/Pt and Ti/ZnO/SRO devices were also measured at 0.1V and room temperature as shown in the left-top insets in Fig.3 (a) and Fig.3 (b), respectively. This demonstrates that no significant change in the resistance occurred in either device, in either the HRS or the LRS, over a period of 12000s.

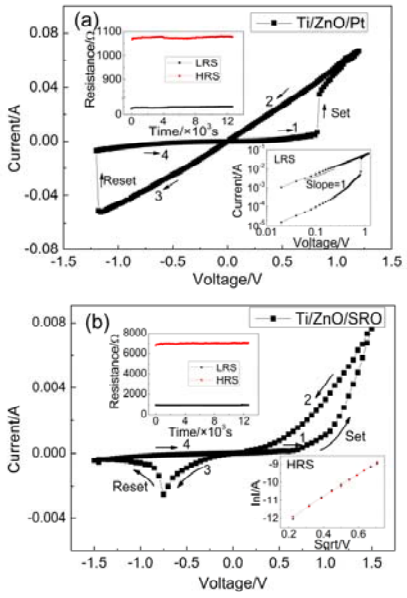


Fig.3 Representative switching behaviours in Ti/ZnO/Pt (a) and Ti/ZnO/SRO (b) devices with the compliance current limited to 100mA. The arrows indicate the voltage sweeping directions. The left-top insets show the retention properties of the two devices. The right-bottom insets show the Log-log scale *I-V* curves in the LRS for the Ti/ZnO/Pt device (a) and ln$I$-$V^{1/2}$ linear fitting in the HRS for the Ti/ZnO/SRO device (b), respectively.

To investigate the effects of the electric field on the magnetism of the ZnO films, we first measured the *M-H* curves for both devices in the initial state (IS) at room temperature. Subsequently, we switched the devices to the LRS and HRS (the initial cycle), and measured their *M-H* curves again. The results for ZnO grown on the Pt and

SRO BEs are shown in Fig.4 (a) and Fig.4 (b), respectively. It may be seen from Fig.4 (a) that for the device with a Pt BE, the magnetic moment in the IS was only 4.19μemu, while it increased to 28.49μemu in the LRS and then dropped to 9.40μemu in the HRS, which are 5.8 and 1.2 times larger than that in the IS. In order to verify the reversibility of the magnetic switching, the device was triggered back to the LRS and HRS again (the second cycle) and the *M-H* curves were re-measured. The results are also shown in Fig.4 (a). It was found that the magnetic moment were reversibly switchable between the HRS and LRS despite the value of the magnetic moment in the second cycle being much less than in the initial cycles. However, from the third cycle on, the value of the magnetic moment in the LRS and HRS remain basically the same as the corresponding values in the second cycle. In other words, there was no longer any obvious reduction of the magnetic moment in the HRS and LRS after the second cycle. The results in Fig.4 (a) are consistent with ref.8 and ref.10 (filamentary type switching).

In contrast, for the ZnO film with an SRO BE, the magnetic switching is the reverse of the switching of the ZnO film grown on the Pt BE. It can be seen from Fig.4 (b) that for the ZnO film with an SRO BE, the magnetism was weak when the device was set to the LRS while the magnetism was strong when the device was reset to the HRS. The value of magnetic moment reached up to about 17.42μemu in the HRS, which is significantly larger than the value of 6.55μemu in the LRS. After the device was retriggered back to the LRS and then to the HRS, the original magnetic moments could be largely restored in both states, suggesting good reproducibility of the magnetism between the HRS and LRS. The results in Fig.4 (b) are consistent with ref.9 (interface switching).

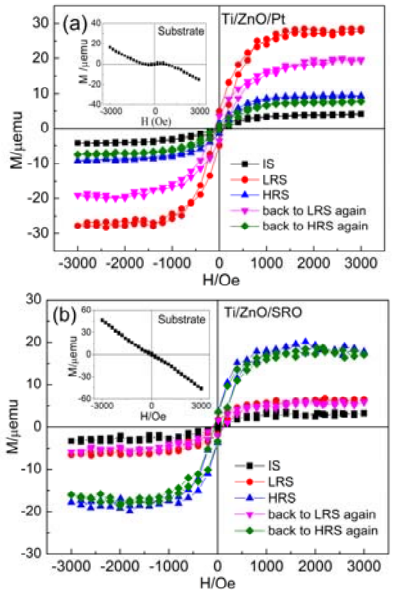


Fig.4 *M-H* curves of Ti/ZnO/Pt (a) and Ti/ZnO/SRO (b) devices in the HRS and LRS. The top insets show the *M-H* curves of the Pt (a) and SRO (b) substrates, respectively.

It is generally accepted that the RS, either of the interfacial or filamentary conduction variety, comes from the migration of $V_O$s in transition-metal oxides under an applied electric field. The magnetism observed in undoped transition-metal oxide films ($d^0$ magnetism) is related to the concentration and distribution of $V_O$s.[17] Since an Ohmic contact is expected in Ti/ZnO interface due to the low work function of Ti and a roughness of about 4 nm of the ZnO film,[18, 19] the chemical properties of the BE materials may play a role on the RS and magnetic switching in un-doped ZnO films. In distinction from the commonly used inert Pt electrode, SRO when used as a BE, can be a supplier of oxygen ions,[20] and thus may have a different influence on the concentration and distribution of Vos thus affect the RS and magnetic switching for the same film.

For the Ti/ZnO/Pt device, there are expected to be a significant number of $V_O$s pre-existing in the as-grown ZnO film due to the deposition conditions with its low oxygen pressure.[10, 21] The initial presence of these $V_O$s can be confirmed by the lack of a forming process[10,13] in the Ti/ZnO/Pt device (see Fig.3(a)). It is well known that metal/semiconductor interfaces are in Ohmic contact in the case of very heavy doping.[22] Consequently, in this device, the Schottky barrier at the ZnO/Pt interface can be eliminated by a sufficiently large number of $V_O$s in the ZnO film and thereby results in an Ohmic contact at the ZnO/Pt interface. When a positive electric field is applied to the TE, the positively charged $V_O$s migrate towards the BE and rapidly form $V_O$-based conducting filaments in the film, switching the device to the LRS. The formation of filaments results in a tremendous increase in the concentration of $V_O$s along the filamentary path across the whole ZnO film, thus leading to more magnetically active polarons producing stronger global ferromagnetism.[23] When a reverse electric field is applied, the $V_O$s migrate back to the TE, which results in partial rupture of the conducting filaments, forcing the film into the HRS. At the same time, the dramatic reduction in the number of $V_O$s in the film results in the weaker film magnetism in the HRS.

For the Ti/ZnO/SRO device, the *I-V* behaviour is consistent with previous reports on the interfacial effects,[15, 20, 24] where the migration of $V_O$s in the vicinity of the interface drives RS.[25] In this device, metallic oxide BE, SRO, may play a role of an oxygen supplier during deposition time.[20] Taking into account that ZnO is n-type semiconductor with $V_O$s, in Pt/ZnO/SRO structure, oxygen diffusion during deposition process might influence defect structures of ZnO near SRO BE resulting in the formation of a thin ZnO layer with poor conductivity near the BE.[20] Therefore, during RS, the applied electric field may be concentrated on ZnO/SRO interface in Pt/ZnO/SRO structure leading to the interface type RS. The formation of this ZnO thin layer with poor conductivity is also supported by the high resistance in both HRS and LRS for Ti/ZnO/SRO device. It can be seen from the left-top inset of Fig.3 that the resistances of about 969 Ω and 6760 Ω in the LRS and HRS for the Ti/ZnO/SRO device are much higher than the corresponding values of 38 Ω and 1060 Ω for Ti/ZnO/Pt device. For this Ti/ZnO/SRO device, the Schottky mechanism arises from the change of the Schottky barrier with electric fields[15, 20, 26]. When a positive bias is applied to the Ti TE, the Vos in the ZnO film would move toward the Schottky-type interface between ZnO/SRO thus the Schottky barrier is reduced and switching the device to the LRS. In this case, the $V_O$s left in the bulk ZnO film are insufficient to form conductive filaments. The lack of $V_O$s in the bulk of ZnO film in the LRS results in the weak magnetism for this device. Under a negative electric field, the Vos migrate away from the ZnO/SRO interface, which causes the Schottky barrier to recover and return the device to the HRS[15]. At the same time, the increase in the number of $V_O$s in the bulk of the ZnO film results in stronger global ferromagnetism of the film.

## Conclusions

In conclusion, electric field control of magnetism was achieved in Ti/ZnO/SRO and Ti/ZnO/Pt devices during resistive switching. For the Ti/ZnO/Pt device, the conduction was dominated by local filamentary conduction, and the magnetic moment in the low resistance state was higher than that in the high resistance state. On the contrary, for the Ti/ZnO/SRO device, dominated by an interfacial Schottky barrier, the magnetic moment was much larger

in the HRS than in the LRS. The different mechanisms of resistive and magnetic switching are considered to be based on the different role played by the Pt and SRO electrodes. Our work suggests that the magnetism of un-doped ZnO film is sensitive to the electric field thus provide a simple method to alter the magnetic properties of the film.

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## Notes and references

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# A table of contents entry

Opposite magnetic switching was achieved in ZnO with different electrodes under electric-field. This can be used to alter the magnetism.