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Enhancement of electrically controlled ferromagnetism in metal-oxide films through magnetic transition metal doping

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ABSTRACT

Large forming voltages, low resistive and magnetic switching ratios and poor reversibility have impeded the practical applications of electrical manipulation of magnetic properties through a resistive switching process. Here we show that all above parameters can be improved greatly through Co doping in Ti/TiO_2/Pt device. A comparison of different mechanism of electrically controlled nonvolatile ferromagnetism in Co-doped and undoped TiO_2 films is proposed. These results will provide a fundamental understanding for the electrically control of ferromagnetism in doped and undoped metal-oxide films and may be extended to certain materials in addition to Co doped TiO_2.

1. Introduction

As one of the most promising candidates for next-generation nonvolatile memories, electrically induced resistive switching (RS) in binary metal-oxide films has attracted increasing attention in recent decades [1,2]. Today, it is widely accepted that the migration of oxygen vacancies (Vos) under an applied electric field leads to the formation/rupture of conductive filaments (CFs), giving rise to the RS effect of the films [1,3–7]. Since the Vos play a crucial role in the room temperature ferromagnetism (FM) of diluted magnetic oxide films [8,9], it may be possible to modulate the FM through electrical control of the local concentration of Vos during RS in these films. In recent years, the electrical manipulation of magnetic properties accompanied by RS has been reported in certain doped and undoped binary metal-oxide films [10,11]. However, the role that the doping elements play in room temperature FM under an applied electric field remains unclear.

As one of the most prospective RS materials, TiO_2 has attracted great attention due to its wide band gap, outstanding thermal stability, high dielectric constant and excellent I-V characteristics [12–14]. However, poor stability and wide variation of set voltage (V_{SET}) and reset voltage (V_{RESET}) in this material impede its application. These effects arise from the random migration of the Vos under an electric field, which hinders formation of a CF along the same path in repetitive switching processes [15,16]. It has been reported [17,18] that metal doping can effectively reduce the Vo formation energy and thus increase the Vo concentration inside the films. Additionally, metal doping also easily forms CFs near the doped metal elements and thus decreases the randomness of the CF generation/rupture process. Hirose et al. [19] reported that the storage window can be enlarged by Co, Mn and Fe doping in TiO_2-based resistive random access memory (RRAM) and that Co doping offers a greater storage window than Mn and Fe doping. The Co dopants serve as chemical anchors for Vos in the development of CF channels and lower the dispersion of switching parameters [20]. Taking into account the importance of Vos and magnetic Co ions played in FM, Co doping may also provide an opportunity to enhance electrically induced nonvolatile FM in TiO_2 films. In this work, we report a comparative study on RS and FM under an electric field in both Co-doped and undoped TiO_2 films. The effect of Co doping on the migration of Vos, the formation of CFs, and the mechanism of electrically controlled nonvolatile FM in Co-doped and undoped TiO_2 films are investigated in detail.

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2. Material and methods

Both TiO_2 and 5 at.% Co-doped TiO_2 ($Co{:}TiO_2$) films were deposited on a $Pt/Ti/SiO_2/Si$ substrate (5 mm × 3 mm × 0.5 mm) using the pulsed laser deposition (PLD) technique from the corresponding stoichiometric targets. After the base pressure of the chamber was reduced to less than 10^{-5}Pa, deposition was performed using a KrF excimer laser ($\lambda = 248$ nm) at 3 Hz with a substrate temperature of 500 °C under an oxygen pressure of 2 Pa. Ti top electrodes with a diameter of 200 μm were deposited with a metal shadow mask in an RF magnetron sputtering instrument. The crystal structure and surface morphology of the films were investigated by X-ray diffraction (XRD, PANalytical X'pert PRO MPD) with Cu Kα radiation and scanning electron microscopy (SEM, Hitachi S-4800), respectively. The current-voltage (I-V) characteristics were measured using a Keithley2612 system at room temperature. During the measurements, the bias voltage was applied across the top electrodes and a grounded Pt bottom electrode. The magnetic measurements were performed using a physical property measurement system (PPMS-6700), and the applied magnetic field was parallel to the films.

3. Results and discussion

The XRD patterns of the TiO_2 and $Co{:}TiO_2$ films are shown in Fig. 1. Only (101) peaks from the anatase structure are observed in both films, and no peaks related to any impurity phases are detected within the XRD detection limits. The (101) peak corresponding to the $Co{:}TiO_2$ film is shifted to a lower angle relative to the TiO_2 film. This shift represents the expansion of lattice parameters in the $Co{:}TiO_2$ film, indicating that Co replaces Ti^{4+} in the form of Co^{2+} rather than Co^{3+} or Co^{4+} because the ionic radius of Co^{2+} (0.072 nm) [21] is greater than the radius of Ti^{4+}(0.068 nm) [22]. The cross-sectional SEM image of the $Co{:}TiO_2$ film is shown in the inset of Fig. 1. The film possesses a columnar structure with a thickness of approximately 100 nm. The microstructure of the TiO_2 film is similar to that of $Co{:}TiO_2$ (not shown).

Fig. 2 shows 30 representative switching loops and retention properties of both $Ti/TiO_2/Pt$ and $Ti/Co{:}TiO_2/Pt$ devices. A forming process is required for both devices. However, the forming voltage for the $Ti/Co{:}TiO_2/Pt$ device is approximately only 0.72 V, which is much lower than the corresponding value of 1.05 V for $Ti/TiO_2/Pt$. It is known that a forming process is usually required for devices without adequate Vos preexisting in the dielectric layer. The effect of the forming process is to generate enough Vos to form complete CFs connecting the two terminal electrodes [23]. The preexistence of a large amount of Vos in the dielectric film eliminates the need for such a forming process [24]. Thus, the large decrease of the forming voltage in the $Ti/Co{:}TiO_2/Pt$ device may indicate that the Vo concentration within the $Co{:}TiO_2$ film is much higher than that in the TiO_2 film. The theoretical calculations in a previous report [25] suggest that the formation energy of the Vos in TiO_2 is greatly reduced through Co doping, which explains the increase of the Vo concentration in the $Co{:}TiO_2$ film in this work. The insets of Fig. 2(a) and (b) show the corresponding V_{SET} and V_{RESET} distribution of both devices. As seen in the inset of Fig. 2(a), the undoped $Ti/TiO_2/Pt$ device shows a wide distribution of V_{SET} and V_{RESET}, which range from 0.32 V to 0.72 V and from −0.72 V to −1.16 V, respectively. The corresponding variations of V_{SET} and V_{RESET} are 0.30 V and 0.44 V, respectively. The inset of Fig. 2(b) shows that the variation of V_{SET} and V_{RESET} for the Co-doped $Ti/Co{:}TiO_2/Pt$ device are only 0.04Vand 0.08 V, respectively. These results demonstrate that the dispersion of switching voltage is reduced remarkably through Co doping; thus, the repeatability of the RS can be greatly improved. In the Co-doped TiO_2 film, the randomness of Vo migration under electric fields is greatly reduced, and the growth of Vo-based CFs may occur along the same paths in different cycles since the Co can serve as a chemical anchor for Vos [20]. Fig. 2(c) shows the retention properties of the devices in the high resistance state (HRS) and the low resistance state (LRS) at a read voltage of +0.1 V. Both devices have satisfactory retention properties, and the states are retained without any degradation after removing the electric field over a period of 12,000s. In addition, it should be noted that the RS ratio (R_{HRS}/R_{LRS}) of the $Ti/Co{:}TiO_2/Pt$ device increases from 38 in $Ti/TiO_2/Pt$ to 100. The increase of the RS ratio in the $Ti/Co{:}TiO_2/Pt$ device is attributed to the large enhancement of R_{HRS} [20,26].

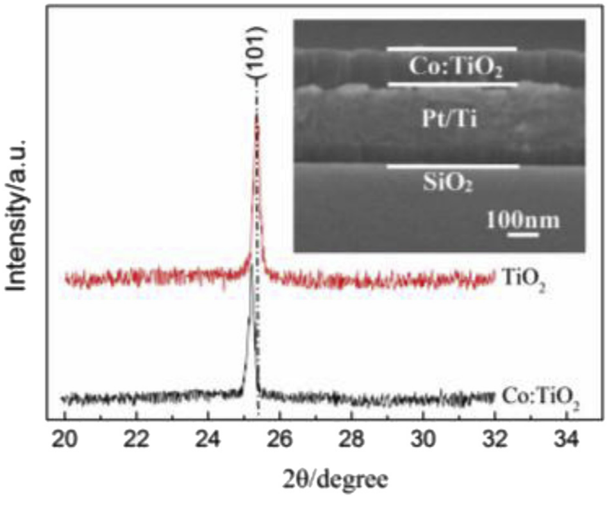

Fig. 1. XRD patterns of TiO_2 and $Co{:}TiO_2$ films. The inset shows the cross-sectional SEM image of the $Co{:}TiO_2$ film.

Fig. 3 shows the magnetic hysteresis loops (M-H curves) for the TiO_2 and $Co{:}TiO_2$ films in three resistive states, including the initial state (IS), LRS and HRS at room temperature (the signal from the substrates has been subtracted). A weak FM with a magnetic moment of 10.9μemu is present for the TiO_2 film in the IS. The corresponding saturation magnetization, Ms is approximately 7.3emu/cm^3, which is consistent with previously reported values for TiO_2 films (7.1emu/cm^3) [11]. After switching to the LRS, the value of the magnetic moment increases to 31.5 lμemu (Ms ≈ 21.3emu/cm^3), which is 2.9 times that in the IS. When the TiO_2 film is reset to the HRS, the Ms decreases to 11.9emu/cm^3. The ratio of M_{LRS}/M_{HRS} is approximately 1.79. The FM in both the LRS and HRS is nonvolatile since the magnetic properties were measured after the electric field was turned off. To confirm the reversibility of electrically controlled magnetism, the magnetic moments obtained from the hysteresis loops for the three consecutive cycles are displayed in the inset of Fig. 3(a). The magnitude of the magnetic moment is switchable between the HRS and LRS, indicating that the magnetism can be modulated reversibly by an external electric field. However, there is an unambiguous reduction of the magnetic moment, particularly in the LRS in the second cycle. This reduction may be due to the formation of complete CFs in the initial cycle while partial rupture and reconnection occurs in later cycles [27].

Fig. 3(b) shows that electrical manipulation of nonvolatile magnetism has also been obtained in the $Co{:}TiO_2$ film. Due to Co doping, the values of magnetic moment reach 67.3μemu (Ms ≈ 45.9emu/cm^3) in the LRS, which is 3.6 times the value of 18.7μemu (Ms ≈ 12.5emu/cm^3) in the IS. The M_s in the HRS is 18.5emu/cm^3, and the M_{LRS}/M_{HRS} ratio is 2.48. It is clear that all the above parameters are much higher than the corresponding values