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Thickness effect on the stability of unipolar resistance switching in tin ferrite thin films

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ABSTRACT

We report the reproducible unipolar resistance switching behavior in Pt/$SnFe_2O_4$/Pt structures. The amorphous $SnFe_2O_4$ thin film was spin-coated on the Pt/TiO_2/SiO_2/Si substrate by a sol-gel method. The current-voltage characterization showed that as the spin coating cycles increased, the resistive switching (RS) characteristics became stable, and an excellent RS performance showing uniform set voltage distribution, stable resistance of both low resistance and high resistance states, and narrow reset current distribution can be obtained in SFO films with a thickness about 220 nm. Based on the conducting filament model, the variation of the RS behavior was ascribed to the increase of the electroforming voltage in the thicker films, which consequently induced more oxygen vacancies to participate in the RS process. Our results indicated that the electroforming voltage performs a significant role in the RS properties of the amorphous $SnFe_2O_4$ and the optimized RS behavior through the regulation of preparation process can be used for the resistance random access memory applications.

1. Introduction

The resistive switching (RS) effect has attracted tremendous attention for its potential applications in realizing the next generation non-volatile memory, i.e., resistive random access memory (RRAM) [1]. The RS device, which possesses a capacitor-like structure composed of a metal-oxide insulator-metal (MIM) sandwiched configuration, can be switched between a low resistance state (LRS) and a high resistance state (HRS) by applying an external electrical stimulation [2]. The switching mechanism has been widely explained by the metallic conducting filament theory through the formation and dissolution of the conductive filament in the insulator layer of the RRAM device, and the direct observation of the conducting filament has been reported [3–5].

A large amount of popular oxide thin films have been studied for its RS performance, including the binary oxides such as NiO [6], HfO_x [7], and ZnO [8]; perovskites such as $Pr_{0.7}Ca_{0.3}MnO_3$ [9], $LaSrMnO_3$ [10], and $BiFeO_3$ [11]. Recently, ferrite materials with the spinel structure are gaining increasing interest for their potential applications in the RRAM device [2,12–15]. Our previous work indicated that Cu doping in $CoFe_2O_4$ can enhance the hopping process between the Fe ions and the Cu ions in the spinel lattice, which can contribute towards the stability of the switching parameters, such as the switching voltage and the resistance in both the high resistance and low resistance states [2]. We have also reported that a more stable RS device without the forming process can be obtained through the changing of the spin-coating times in the $CoFe_2O_4$ thin films, which could provide meaningful insights in achieving stable and forming-free switching in the ferrite material-based resistance switching memory devices [15].

Since most ferrite materials exhibit interesting magnetic properties together with insulating electrical behaviors, the investigation of the RS properties in ferrite-based materials can promise the development of multi-state memory devices through magnetic and electrical regulations in one material [2,13–17]. It is therefore important to explore new ferrite-based RS materials and elucidate the conducting mechanism. It has been reported that more oxygen vacancies could be generated in the spinel ferrites such as $NiFe_2O_4$ and $CoFe_2O_4$ due to the tunable valence states of the transition metals ($Fe^{+2/+3}$, $Co^{+2/+3}$, and $Ni^{+2/+3}$) [14], and the oxygen vacancies will dominate the RS effect in these thin films [12,14]. In addition, it has been reported that tin ions can exist as Sn^{+2} and Sn^{+4} in tin doped nanocrystalline $CoFe_2O_4$, and the fluctuation of the valence states ($Sn^{+2} \leftrightarrow Sn^{+4} + 2e^{-1}$) can lead to an increasing

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conductivity in the tin doped system [18]. Thus, the investigation of tin ferrite [$SnFe_2O_4$·(SFO)]-based RS materials to elucidate the conducting mechanism will provide meaningful insights to the development of spinel ferrites-based RS memory devices.

SFO is a paramagnetic inverse spinel oxide with both of its constituent metal elements, i.e., Sn and Fe, being relatively earth-abundant [19]. Nanostructured SFO has been synthesized using different techniques such as solvent-assisted interfacial reaction [19], precipitation exchange [20,21], ball milling [22], and co-precipitation methods [18,23,24]. However, previous works on SFO were mainly focused on its magnetic property [18,20,21,24] and the photocatalytic performance [19,23]. RS properties of SFO has been rarely reported yet. In this work, we have successfully prepared SFO thin films on the $Pt/TiO_2/SiO_2/Si$ substrates using a sol-gel method, and stable resistive switching with low-power consumption was achieved in SFO thin films with a suitable thickness.

2. Experiment

The SFO thin films were prepared by the sol-gel method on the $Pt/TiO_2/SiO_2/Si$ substrates. To prepare the SFO thin films, $SnCl_2$ and $Fe(NO_3)_3·9H_2O$ were first separately dissolved in 2-methoxyethanol as the precursor solutions, and then mixed together with a molar ratio of Sn:Fe = 1:2. The mixed solution with a Sn^{+2} concentration of 0.2 M was stirred on a hot plate for 4 h at room temperature and then was left to stand for 14 h before use. In order to improve the wetting property of the surface, the substrates were first cleaned in a mixture of ammonia and peroxide at 75 °C for 15 min, and then in a mixture of hydrochloric acid and peroxide at 70 °C for 15 min. The SFO thin films were deposited on the $Pt/TiO_2/SiO_2/Si$ substrates by spin-coating, with a rotational speed of 3000 rpm for 30 s. After each coating, the films were first dried at 120 °C for 10 min to evaporate the solvent, and then pre-annealed at 400 °C for 10 min to exclude the organic residuals. The spin-coating and pre-annealing process were repeated until the desired film thickness was achieved. In this work, the thickness of the SFO films was varied from 3 to 5 layers, which were labeled as SFO-3, SFO-4, and SFO-5, accordingly. Finally, the deposited films were post-annealed at 600 °C for 1 h in the ambient air. To fabricate the Pt/SFO/Pt structure, 100-nm-thick Pt top electrodes were deposited on the SFO films by e-beam evaporation. The top electrode size was 90 × 90 μm.

The crystalline phase of the thin films was characterized in θ-2θ mode by Rigaku X-ray diffraction (XRD) with a Cu K_α radiation. The surface and cross sectional morphology of the thin films were observed by the scanning electronic microscopy (SEM). The chemical states were characterized by the X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed using a monochromated Al K_α X-ray source (hv = 1486.6 eV) at 15 kV/150 W. The spot size used was 400 μm (Theta Probe AR-XPS System, Thermo Fisher Scientific, Waltham, MA, USA). The current-voltage (I-V) characteristics of the Pt/SFO/Pt structure was investigated using a semiconductor device analyzer (Agilent Technologies B1500A) with two probes.

3. Results and discussion

The SFO films spin-coated with different thicknesses were concluded to be amorphous since the X-ray diffraction spectra did not show any distinctive pattern (data not shown). Fig. 1(a) shows the surface morphology of the amorphous SFO-5 film. It can be seen that the surface of the SFO-5 film was flat and no grains were observed, which supports that the SFO thin films were amorphous. The thickness of the SFO-5 thin film is approximately 220 nm

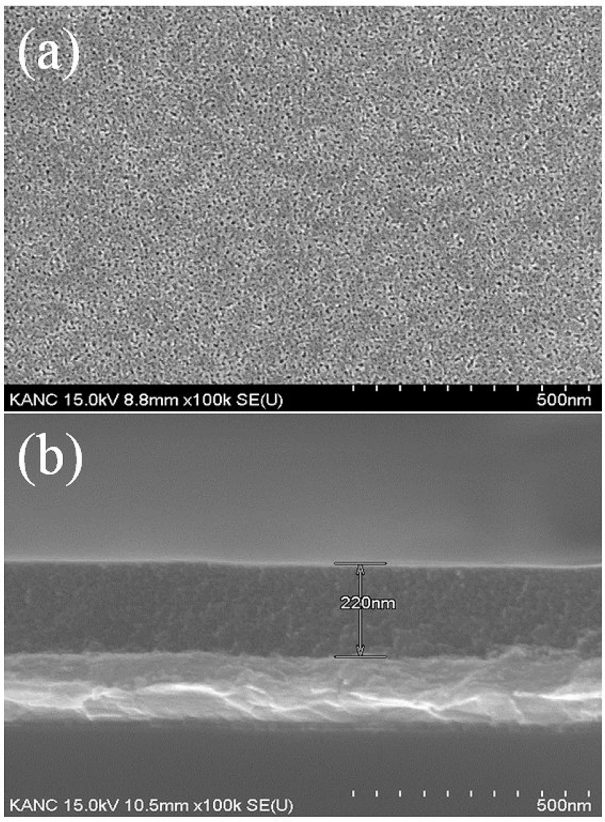

Fig. 1. SEM images of the SFO-5 film. (a) Surface morphology; (b) Cross-sectional morphology of the film.

according to the cross-sectional image shown in Fig. 1(b). The thicknesses of the SFO-3 and SFO-4 thin films prepared with different spin coating cycles were also measured using SEM, and it was found that the average thickness of each coating is 45 ± 1 nm, and the thickness of the SFO thin film increased almost linearly with the number of spin-coating cycles.

To determine the valence states and the degrees of oxidation of the Sn, Fe, and O elements in the amorphous SFO thin films, XPS characterization was performed. Fig. 2(a) displays the XPS survey scan of the SFO-5 thin film, which reveals the existence of the C, Sn, Fe, and O elements. The Sn 3d spectrum was shown in Fig. 2(b) along with the fitting results. The best fit to the Sn $3d_{5/2}$ resulted into two separate peaks at 485.6 eV and 486.1 eV, which confirmed the coexistence of Sn^{+2} and Sn^{+4} [25]. Similarly, we found that the Sn $3d_{3/2}$ peak can also be divided into two peaks having binding energies at 494.0 eV and 494.5 eV, which were consistent with the binding energies of Sn^{+2} and Sn^{+4} separately [25]. Fig. 2(c) shows the spectrum of Fe 2p. The oxidation state of Fe^{+3} was revealed from the two peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ located at the binding energy of 710.8 eV and 724.3 eV, respectively, with a separation between Fe$2p_{3/2}$ and Fe $2p_{1/2}$ about 13.4 eV [26,27]. The analysis of the O 1s peak can be de-convoluted into three peaks: the main peak at 529.5 eV, which corresponds to the structural oxygen, the medium binding energy peak located at 529.9 eV, which represents the oxygen deficiencies/vacancies in the amorphous SFO, and the third component with an even higher binding energy of 531.2 eV, which usually belongs to the adsorbed oxygen on the surface of the SFO-5 film [28–30].

Since the as-prepared $SnFe_2O_4$ films always showed a high initial resistance, an electroforming process using a threshold current pulse of 2 mA was performed on the device to investigate the