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Regulation of the forming process and the set voltage distribution of unipolar resistance switching in spin-coated CoFe_2O_4 thin films

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Abstract

We report the preparation of (111) preferentially oriented CoFe_2O_4 thin films on Pt(111)/ $\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates using a spin-coating process. The post-annealing conditions and film thickness were varied for cobalt ferrite (CFO) thin films, and Pt/CFO/Pt structures were prepared to investigate the resistance switching behaviors. Our results showed that resistance switching without a forming process is preferred to obtain less fluctuation in the set voltage, which can be regulated directly from the preparation conditions of the CFO thin films. Therefore, instead of thicker film, CFO thin films deposited by two times spin-coating with a thickness about 100 nm gave stable resistance switching with the most stable set voltage. Since the forming process and the large variation in set voltage have been considered as serious obstacles for the practical application of resistance switching for non-volatile memory devices, our results could provide meaningful insights in improving the performance of ferrite material-based resistance switching memory devices.

Keywords: Resistance switching; CoFe_2O_4 ; Set voltage; Forming process

Background

Resistance random access memory (RRAM), which is based on the resistance switching (RS) phenomenon in oxide thin films, has attracted much attention due to its potential applications in the next generation non-volatile memory. RRAM have been demonstrated to exhibit excellent miniaturization potential down to less than 10 nm [1], sub-ns operation speed [2,3], energy consumption (<0.1 pJ) [4,5], and high endurance (> 10^{12} switching cycle) [6]. Resistance switching (RS) behavior has been reported in many oxide material-based metal/oxide/metal (MOM) structures. When the MOM structure is electrically stimulated by either a current or voltage, the resistance of the MOM structure can be switched between a high resistance state (HRS) or '0' and a low resistance state (LRS) or '1'. Popular oxide thin films that have been studied for RRAM applications include binary oxides such as NiO [7], TaO_x [8], and HfO_2 [9], perovskites such as $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ [10], $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [11], and BiFeO_3 [12]. For unipolar

resistance switching (URS), the SET and RESET processes, which refer to the switching of the MOM structure from a HRS to a LRS and *vice versa*, respectively, can be induced by an applied voltage regardless of its polarity. The switching mechanism has been studied intensively, and the formation and rupture of metallic conducting filaments (CFs) have been generally accepted to explain the switching between the HRS and LRS [13].

Recently, spinel ferrites have gained interest as a potential material for RRAM applications [14-17]. Spinel ferrites have the general formula of AFe_2O_4 , where A represents one or more divalent metal ions. Ag/ ZnFe_2O_4 /Pt structure has been reported to show RS due to the formation of CFs consisting of metallic Ag and oxygen vacancies [14]. Effort has also been paid to investigate the relation between the resistance state and the magnetic properties using Pt/ NiFe_2O_4 /Pt structures, and the results showed that the difference in the hysteresis loops at HRS and LRS was actually quite small [15]. Ag/ NiFe_2O_4 /Pt and Ag/ CoFe_2O_4 /Pt structures were reported to have RS if the films were annealed in vacuum, while no RS was found in films annealed in oxygen,

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indicating that oxygen vacancies played an important role [16].

Cobalt ferrite (CoFe_2O_4 , CFO) is an important member of spinel ferrites and has gained much interest due to its rich unique magnetic and electronic properties such as magneto-optic and magneto-electric effects [17,18]. Since ferrite materials exhibit ferromagnetic behaviors but are electrically insulating, it is possible to explore both magnetic and resistance regulations in one material. Sol-gel-derived CFO and sputtering-deposited CFO thin films have been investigated for their RS properties, and the reported results mainly focused on the conduction mechanisms in the HRS and LRS [16,19]. The Pt/CFO/Pt structure has been reported to show URS with high retention capability and no detectable degradation for more than 10^4 s [19].

In this work, we prepared CFO thin films with spin-coating and studied the effect of post-annealing conditions and film thickness on the RS properties of Pt/CFO/Pt structure. The purpose of this study is to eliminate the forming process and to reduce the set voltage (V_{SET}) fluctuation normally observed in RRAM devices by regulating the preparation conditions of oxide thin films. For most RRAM devices, the oxide thin film is originally insulating so that a so-called ‘forming process’ is necessary to induce a soft breakdown by generating CFs in the oxide. This forming process usually occurs at a much higher voltage than V_{SET} , which leads to high power consumption and circuit complexity. V_{SET} refers to the voltage value that the SET process occurs, i.e., the device is switched from a HRS to a LRS. Due to the intrinsic randomness during the formation of CFs in an insulating oxide thin film, V_{SET} usually has a quite wide distribution and has been considered as a serious issue to be overcome before practical applications [13]. Up to now RS behaviors in CFO thin films requiring no forming process has rarely been reported, possibly due to the quite high resistance of bulk CFO. Regarding the effect of deposition conditions on the V_{SET} distribution, higher annealing temperature has been shown to reduce the fluctuation of set voltages in sol-gel-prepared BiFeO_3 [12]. Our results show that the preparation conditions of CFO thin films, i.e., post-deposition annealing temperature and film thickness, can be optimized to obtain stable RS behavior requiring no forming process, i.e., forming-free (FF) switching, and with less variation in V_{SET} .

Methods

The CFO thin films were prepared using a sol-gel method. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were separately dissolved in 2-methoxyethanol, then the precursor solutions were mixed together with a molar ratio of Co:Fe = 1:2. The mixed solution with a total metal ion

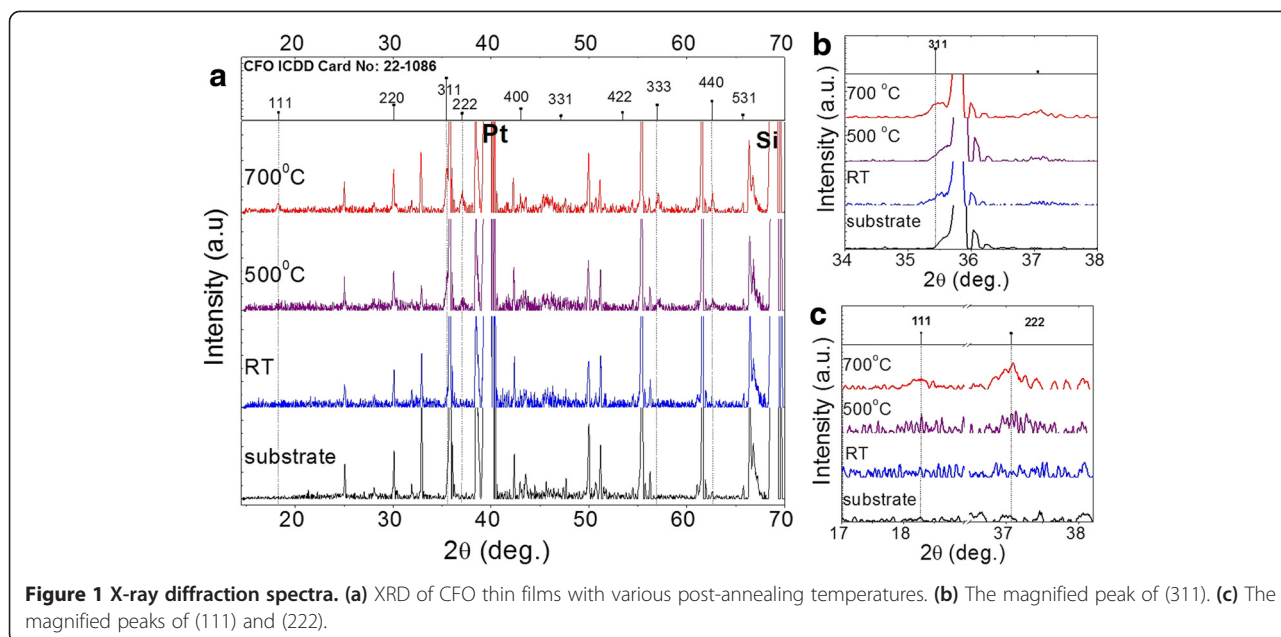
concentration of 0.2 M was then spin-coated on a Pt (111)/ TiO_2 / SiO_2 /Si substrate with a rotational speed of 3,000 rpm for 30 s. After each coating, the films were dried at 170°C for 10 min and then pre-annealed at 400°C for 10 min. The procedures from coating to pre-annealing were repeated up to the desired thickness. More detailed preparation procedures have been reported previously [20]. The CFO thin films were then exposed to different heat treatment process, i.e., no further annealing (CFO-RT), post-annealed at 500°C (CFO-500) or 700°C (CFO-700) for 1 h in air ambient. To fabricate the Pt/CFO/Pt structure, 100-nm-thick Pt top electrodes were deposited on the CFO films by e-beam evaporation. The top electrode size was 90×90 μm .

The crystalline structure and preferential orientation of the films were characterized using the $\theta - 2\theta$ scan by Rigaku X-ray diffraction (XRD) with a Cu radiation. The current-voltage (I - V) characteristics were measured using a semiconductor parameter analyzer (Agilent B1500A; Agilent Technologies, Sta. Clara, CA, USA). During the measurement, the Pt bottom electrode was grounded, and a bias voltage was applied to the top electrode.

Results and discussion

Figure 1a shows the XRD patterns of the CFO with different heat treatment process. All CFO films were spin-coated three times. Weak diffraction peaks that indicate the formation of spinel CoFe_2O_4 started to appear in the XRD spectrum of CFO-500, and all peaks were enhanced in CFO-700. No additional peak except that from the substrate was observed from CFO-RT, indicating that the film without post-annealing was amorphous. For polycrystalline ferrite materials, the main diffraction usually appears as the (311) peak. Figure 1b showed the magnified spectra around the (311) peak, and it is clear that CFO-700 has a better crystallinity than other samples. Furthermore, we observed the (111), (222), and (333) peaks clearly in CFO-700 (Figure 1c), although these peaks normally are not seen in polycrystalline bulk CFO due to their low intensities as compared to other peaks. This preferential orientation in the (111) direction could be induced by the Pt(111) substrates. The small lattice mismatch between CoFe_2O_4 and Pt induced the nucleation of CFO grains with preferred (111) orientation on top of the (111)-oriented Pt substrate [21].

Figure 2 depicts the typical I - V characteristics of the as-fabricated Pt/CFO/Pt structures measured at low bias voltages. Based on the change in the slope of the I - V curve, it is clear that the initial resistance of the device has been significantly affected by the post-deposition heat treatment of the CFO thin films. The initial resistance of the Pt/CFO-RT/Pt structure is about 10 M Ω , and this value decreased to approximately 4 M Ω for

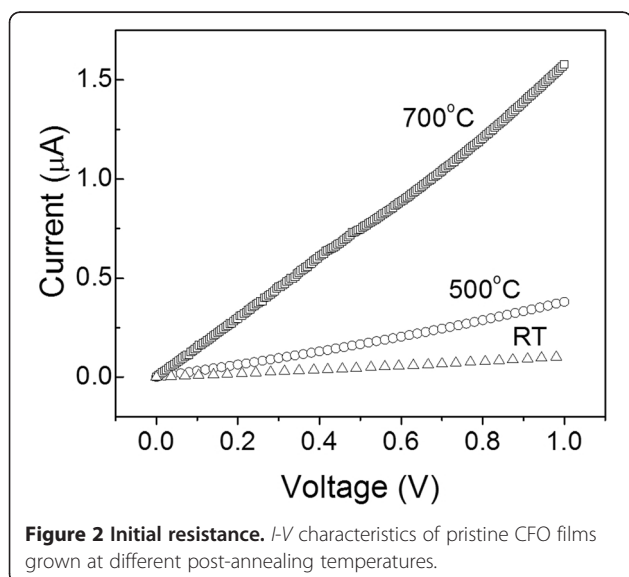


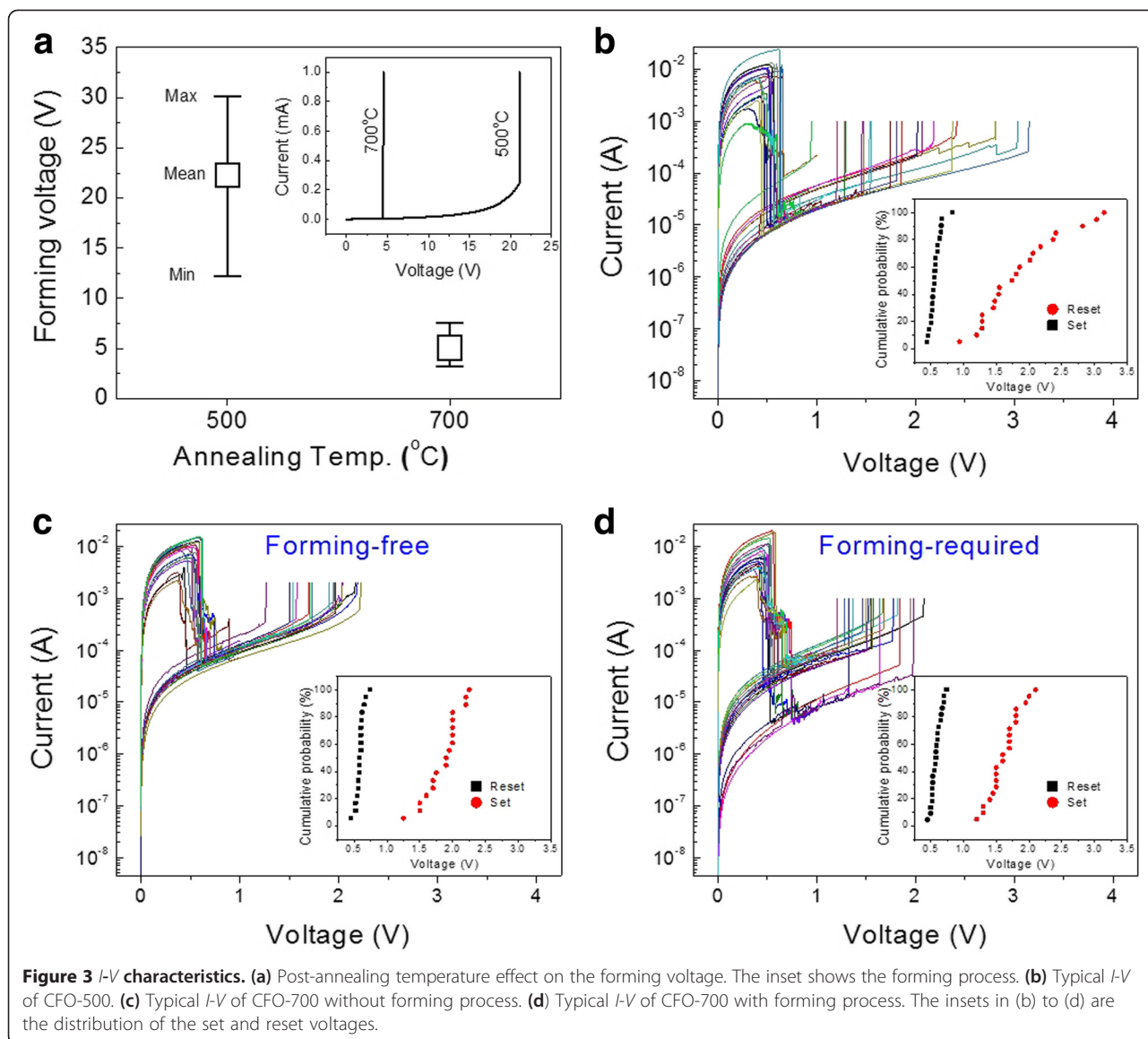
Pt/CFO-500/Pt and 2 MΩ for Pt/CFO-700/Pt. Furthermore, about 17% of Pt/CFO-700/Pt showed even smaller resistance approximately 50 Ω (data not shown).

The RS properties of the Pt/CFO/Pt structures were directly affected by their initial resistance. Pt/CFO-RT/Pt did not show resistive switching, presumably due to the very high initial resistance to initiate soft breakdown inside the film. URS was observed from both Pt/CFO-500/Pt and Pt/CFO-700/Pt, but the stability and reproducibility of RS were much better in Pt/CFO-700/Pt. Although the Pt/CFO-500/Pt structures showed unipolar RS, most devices could no longer be switched after just a couple of switching cycles. Additionally, the forming voltage of Pt/CFO-500/Pt was much larger as compared

to Pt/CFO-700/Pt as shown in Figure 3a. The average forming voltage of Pt/CFO-500/Pt was around 20 V with a wide distribution, whereas the forming voltage of most Pt/CFO-700/Pt was about 5 V. The lower initial resistance and forming voltage observed in Pt/CFO-700/Pt could be a result of increased oxygen vacancies and less grain boundaries. In addition to the improved crystallinity evidenced by the XRD result (Figure 1), a higher growth temperature or annealing temperature has been reported to induce a higher oxygen vacancy concentration in oxide thin films prepared by pulsed laser deposition or sol-gel [12,22]. The oxygen vacancies are known to form and migrate predominantly along the grain boundaries [23]; therefore, the existence of more oxygen vacancies and less randomly distributed grain boundaries seems to facilitate the formation of CFs, resulting in a lower forming voltage in CFO-700.

The RS *I-V* curves of one Pt/CFO-500/Pt device which showed repeated switching are shown in Figure 3b. The reset voltages (V_{RESET}) are quite uniform (0.5 ~ 0.75 V), whereas the range of the V_{SET} are much broader (1 ~ 3.2 V) as seen in the inset of Figure 3b. For Pt/CFO-700/Pt, two types of RS behaviors regarding the forming process were observed. The devices which have low initial resistance approximately 50 Ω can be switched directly from LRS to HRS; therefore, no forming process was necessary. This FF URS switching *I-V* characteristics is shown in Figure 3c. Those devices with higher initial resistance around MΩ, however, required a forming process to initiate RS. The typical forming-required (FR) URS *I-V* curves are shown in Figure 3d. Besides the difference in forming process, a comparison between the set voltages of Pt/CFO-500/Pt and Pt/CFO-700/Pt (inset

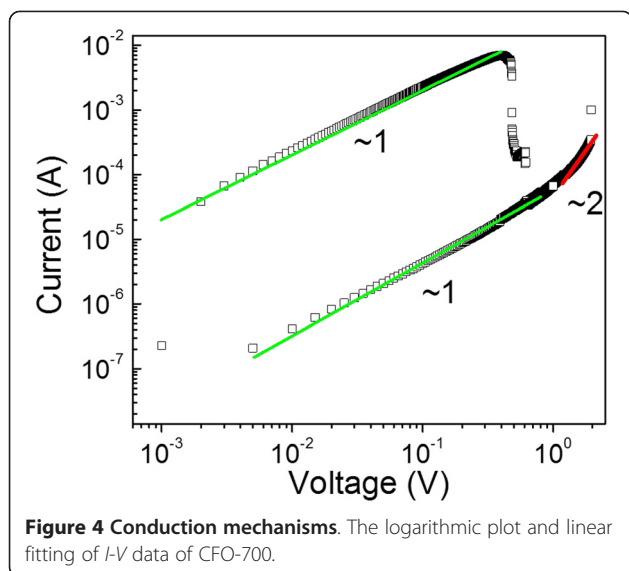




of Figure 3b, c, and d) clearly shows that the distribution of the V_{SET} is much smaller in Pt/CFO-700/Pt. Therefore, considering the forming process and the switching stability, we chose Pt/CFO-700/Pt for further investigation on the RS properties.

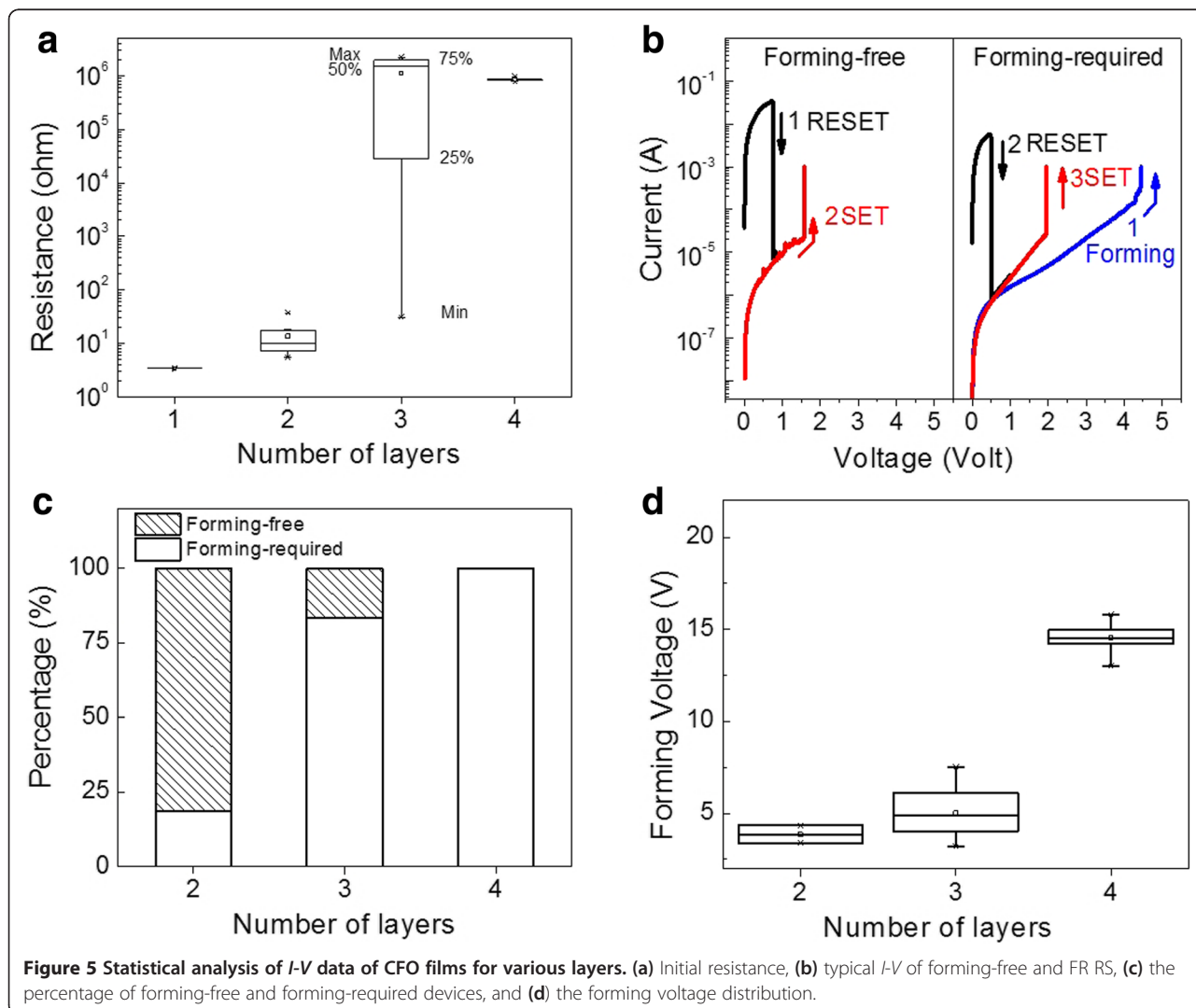
To understand the conduction mechanisms of CFO thin films, the *I-V* curves of the Pt/CFO-700/Pt devices at HRS and LRS were plotted in a log-log scale as shown in Figure 4. In the LRS, *I-V* curves exhibited a linear dependence on voltage with a slope of nearly 1, which satisfies the ohmic behavior. This is thought to correspond to the formation of metallic CFs during the SET process. However, the conduction mechanism of HRS is more complicated. The fitting results suggested that the leakage current at the lower voltage region showed a linear dependence on voltage, whereas at voltages higher than

0.7 V, the current exhibited a dependence on the square of voltage. Accordingly, the conduction mechanisms of HRS can be explained as follows. For the bias voltage less than 0.7 V, thermally generated charge carriers dominated the conduction and followed the ohmic law. When the bias voltage increased, injected carriers started to increase. However, oxygen vacancies or other defects existed in CFO could behave as traps and capture the injected carriers [16,19]. The square law shown for voltages higher than 0.7 V implied that under this condition, the traps in the CFO thin films were almost filled and the *I-V* characteristics were governed by a trap-free space-charge limited (SCL) conduction [24]. Similarly, RS behaviors in $ZnFe_2O_4$ and other reported $CoFe_2O_4$ thin films have also been suggested to follow the SCL conduction at high field in the HRS [14,16,25].



In addition to the heat treatment effect, we further studied the dependence of RS behavior on the thickness of the CFO thin film. From our previous work [20], the thickness of the CFO films post-annealed at 700°C was about 50 to 60 nm for one-time spin-coating, and the CFO thin film thickness increased almost linearly with the number of coating layers. In this work, the thickness of the CFO films was varied by adjusting the number of spin-coated layers from 1 to 4, and the CFO films were labeled as CFO-1, CFO-2, CFO-3, and CFO-4 accordingly.

The initial resistance of CFO with various layers is displayed in Figure 5a. With increasing thickness, the initial resistance increased from the order of $10^0 \Omega$ for CFO-1 up to the order of $10^6 \Omega$ for CFO-4. Accordingly, different RS behaviors were observed from the CFO thin film depending on their thickness. CFO-1 did not show RS due to its much lower resistance that could not be switched to a HRS. From CFO-2 to CFO-3, both FF and FR RS were observed, and the typical switching characteristics are



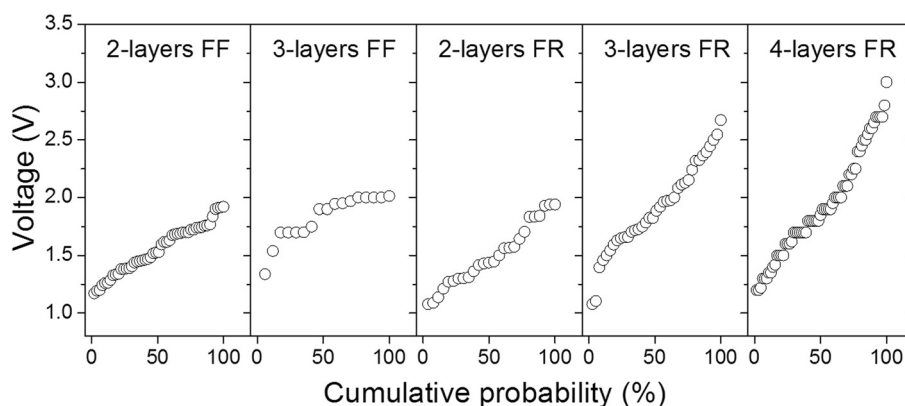


Figure 6 The distribution of set voltages vs. layer numbers and forming behaviors.

shown in Figure 5b. Due to the range of the initial resistance in CFO-2 and CFO-3, the devices with low resistance exhibited the FF switching, whereas the devices of high initial resistance started the FR switching with a forming process. Interestingly, the percentage of the FF and FR devices changed with the CFO film thickness, as shown in Figure 5c. Nearly 80% of the Pt/CFO-2/Pt devices showed FF switching, but the percentage decreased to about 20% in the Pt/CFO-3/Pt devices. This result is in a good agreement with the distribution of the initial resistance illustrated in Figure 5a, considering the relatively lower initial resistance of Pt/CFO-2/Pt and the wide-ranged initial resistance of Pt/CFO-3/Pt overlapped with Pt/CFO-2/Pt. When the CFO thin film was spin-coated four times, all devices showed FR switching, which can be attributed to the higher initial resistance due to increased film thickness. For all FR devices with different CFO film thicknesses, we observed that the forming voltage showed an increasing tendency with the film thickness (Figure 5d), which is also consistent with the results shown in Figure 5a.

The diversity in the forming process and the CFO film thickness were found to have a significant effect on the distribution of the V_{SET} , which has been considered as an important parameter in evaluating the performance of an RRAM device. The V_{SET} distribution dependence on the CFO film thickness and the forming behavior were plotted in Figure 6. The data taken in Figure 6 were taken from multidevices on each film. Regarding the CFO film thickness, it is obvious that the V_{SET} has a much wider distribution in Pt/CFO-4/Pt devices. Furthermore, the FF devices of Pt/CFO-3/Pt structures showed a significant narrowing in the range of the V_{SET} as compared to the FR devices. The FF devices usually have a low initial resistance due to the large amount of pre-existed CFs in the oxide thin films [23]. The FF RS starts with a RESET process that switches the device from the LRS to the HRS, rupturing some of the pre-

existed CFs. During the SET process which switches the device from HRS back to the LRS, the CFs are regenerated preferentially along similar paths; therefore, the V_{SET} shows less fluctuation. On the other hand, the FR devices usually require higher and wider ranged set voltages to reconnect the CFs due to the insulating nature of the oxide film [8]. In this point of view, it is preferred to use Pt/CFO-2/Pt structures for RRAM applications because most of the CFO-2 based devices are FF with a narrowly distributed V_{SET} , as shown in the first two panels of Figure 6. In this case, reduced power consumption and better operation stability can be expected due to the elimination of the forming process and less variation in the V_{SET} .

Conclusions

We have prepared CFO thin films on Pt/TiO₂/SiO₂/Si substrates using spin-coating with various post-annealing conditions and film thickness. Pt/CFO/Pt structures were fabricated using these CFO thin films to investigate the RS properties. Reproducible URS was observed only from CFO thin films post-annealed at 700°C, and the LRS and HRS can be explained with the ohmic conduction and SCL conduction mechanisms, respectively. The thickness dependence investigation revealed that RS started to appear from the Pt/CFO-2/Pt structures and was dominated by the FF switching. With increasing CFO film thickness, FR switching became dominant. Due to the large amount of pre-existed conducting filamentary paths in the FF RS devices, the V_{SET} was found to be more stable than in the FR RS devices; therefore, the Pt/CFO-2/Pt structure was preferred for potential practical RRAM applications.

Abbreviations

CF: conducting filament; CFO: cobalt ferrite; FF: forming-free; FR: forming-required; HRS: high resistance state; LRS: low resistance state; RRAM: resistance random access memory; RS: resistance switching; SCL: space-charge limited; XRD: X-ray diffraction.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MM carried out the structural analysis, *I-V* measurement, and drafted the manuscript. PY participated the film preparation. WH and BW participated in the discussion of the study. CL designed and supervised the whole study. All authors read and approved the final manuscript.

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References

- Ho C, Hsu C-L, Chen C-C, Liu J-T, Wu C-S, Huang C-C, et al. 9 nm half-pitch functional resistive memory cell with 1 μ a programming current using thermally oxidized substoichiometric WO_x film. *IEDM Tech. Dig.*, 2010; 436; doi:10.1109/IEDM.2010.5703389.
- Torrezan AC, Strachan JP, Medeiros-Ribeiro G, Williams RS. Sub-nanosecond switching of a tantalum oxide memristor. *Nanotechnology*. 2011;22:485203.
- Choi BJ, Torrezan AC, Norris KJ, Miao F, Strachan JP, Zhang M-X, et al. Electrical performance and scalability of Pt dispersed SiO₂ nanometallic resistance switch. *Nano Lett.* 2013;13:3213.
- Cheng CH, Tsai CY, Chin A, Yeh FS. High performance ultra-low energy RRAM with good retention and endurance. *IEDM Tech. Dig.* 2010; 448; doi:10.1109/IEDM.2010.5703392.
- Govoreanu B, Kar GS, Chen Y-Y, Paraschiv V, Kubicek S, Fantini A, et al. 10 \times 10 nm² Hf/HfO_x crossbar resistive RAM with excellent performance, reliability and low-energy operation. *IEDM Tech. Dig.*, 2011; 729; doi:10.1109/IEDM.2011.6131652.
- Lee MJ, Lee CB, Lee D, Lee SR, Chang M, Hur JH, et al. A fast, high-endurance and scalable non-volatile memory device made from asymmetric Ta₂O_{5-x}/TaO_{2-x} bilayer structures. *Nat Mater.* 2011;10:625–30.
- Yoo IK, Kang BS, Park YD, Lee MJ, Park Y. Interpretation of nanoscale conducting paths and their control in nickel oxide (NiO) thin films. *Appl Phys Lett.* 2008;92:202112.
- Kurnia F, Liu C, Jung CU, Lee BW. The evolution of conducting filament in forming-free resistive switching Pt/TaO_x/Pt structure. *Appl Phys Lett.* 2013;102:152902.
- Wang Y, Liu Q, Long S, Wang W, Wang Q, Zhang M, et al. Investigation of resistive switching in Cu-doped HfO₂ thin film for multilevel non-volatile memory applications. *Nanotechnology*. 2010;21:045202.
- Kim DS, Kim YH, Lee CE, Kim YT. Resistive switching characteristics of Pr_{0.7}Ca_{0.3}MnO₃ thin films grown on glass substrates by pulsed laser deposition. *Thin Solid Films.* 2006;515(4):2573–6.
- Lee JM, Choi HJ, Seong DJ, Yoon JS, Park JB, Jung SJ, et al. The impact of Al interfacial layer on resistive switching of La_{0.7}Sr_{0.3}MnO₃ for reliable ReRAM applications. *Microelectronic Engineering.* 2009;86:1933–5.
- Zhu X, Zhuge F, Li M, Yin K, Liu Y, Zuo Z, et al. Microstructure dependence of leakage and resistive switching behaviours in Ce-doped BiFeO₃ thin films. *J Physics D Appl Phys.* 2011;44:415104.
- Chae SC, Lee JS, Kim S, Lee SB, Chang SH, Liu C, et al. Random circuit breaker network model for unipolar resistance switching. *Adv Mat.* 2008;20:1154–9.
- Hu W, Chen X, Wu G, Lin Y, Qin N, Bao D. Bipolar and tri-state unipolar resistive switching behaviors in Ag/ZnFe₂O₄/Pt memory devices. *Appl Phys Lett.* 2012;101:063501.
- Hu W, Qin N, Wu G, Lin Y, Li S, Bao D. Opportunity of spinel ferrite materials in nonvolatile memory device applications based on their resistive switching performances. *J Am Chem Soc.* 2012;134:14658–61.
- Jin C, Zheng DX, Li P, Mi WB, Bai HL. Resistive switching in reactive cosputtered MFe₂O₄ (M = Co, Ni) films. *Appl Surf Sci.* 2012;263:678–81.
- Gao XS, Bao DH, Birajdar B, Habisreuther T, Mattheis R, Schubert MA, et al. Switching of magnetic anisotropy in epitaxial CoFe₂O₄ thin films induced by SrRuO₃ buffer layer. *J Phys D Appl Phys.* 2009;42:175006.
- Huang W, Zhu J, Zeng HZ, Wei XH, Zhang Y, Li YR. Strain induced magnetic anisotropy in highly epitaxial CoFe₂O₄ thin films. *Appl Phys Lett.* 2006;89:262506.
- Hu W, Zou L, Chen R, Xie W, Chen W, Qin N, et al. Resistive switching properties and physical mechanism of cobalt ferrite thin films. *Appl Phys Lett.* 2014;104:143502.
- Mustaqima M, Lee MY, Kim DH, Lee BW, Liu C. Growth of textured CoFe₂O₄ thin films on platinized silicon prepared by a sol-gel method. *J Magnet.* 2014;19(3):227–31.
- Seifikar S, Tabei A, Sachet E, Rawdanowicz T, Bassiri-Gharb N, Schwartz J. Growth of (111) oriented NiFe₂O₄ polycrystalline thin films on Pt (111) via sol-gel processing. *J Appl Phys.* 2012;112:063908.
- Kurnia F, Hadiywarman, Jung CU, Jung R, Liu C. Composition dependence of unipolar resistance switching in TaO_x thin films. *Phys Status Solidi RRL.* 2011;7:253–5.
- Park C, Jeon SH, Chae SC, Han S, Park BH, Seo S, et al. Role of structural defects in the unipolar resistive switching characteristics of Pt/NiO/Pt structures. *Appl Phys Lett.* 2008;93:042102.
- Kao KC, Hwang W. *Electrical transport in solid.* Oxford, New York, Toronto, Sydney, Paris, Frankfurt: Pergamon; 1981. p. 150–3.
- Jiang C, Wu L, Wei WW, Dong C, Yao J. The resistive switching memory of CoFe₂O₄ thin film using nanoporous alumina template. *Nanoscale Res Lett.* 2014;9:584.

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