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Cobalt ferrite as an active material for resistive random-access memory

KETANKUMAR GAYAKVAD[1,2] and K K PATANKAR[2,3],*

[1]K.J. Somaiya College of Science and Commerce, Mumbai 400 077, India
[2]Composite Material Laboratory, Rajaram College, Kolhapur 416 004, India
[3]Department of Physics, Rajaram College, Kolhapur 416 004, India
*Corresponding author. E-mail: ketakiketan@gmail.com

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Abstract. Cobalt ferrite is one of the candidates from spinel ferrite family and can be termed as an active material in resistive random-access memory (RRAM) cell because of its excellent performance in switching devices. In this article, the review on the role of cobalt ferrite as an active insulator material for metal/insulator/metal (M/I/M) configuration is discussed. The mode of metal/$CoFe_2O_4$/metal memory cell depends on the electrode material. The metal/$CoFe_2O_4$/metal memory cell exhibits either unipolar resistive switching or bipolar resistive switching characteristics. The switching mechanism of the metal/$CoFe_2O_4$/metal memory cell can be well understood using conducting filament model. The review suggests that the switching cycle characteristics can be improved by proper choice of electrodes, synthesis technique and thickness of the active material thin film.

Keywords. Active material; conducting filament model; electrode; metal/insulator/metal; resistive random-access memory.

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1. Introduction

Resistive random-access memory (RRAM) is one of the emerging RAMs having potential advantages over dyanamic RAM, hard disk, static RAM, flash memory and CD memory. Other equally competent memories are FRAM (ferroelectric RAM), MRAM (magnetic RAM) and PRAM (phase change RAM). However, RRAM is accompanied with good scalability, high endurance, excellent retention, fast operating speed, low power consumption and excellent resistive switching [1,2]. Structure of RRAM is shown in figure 1.

It is a two-terminal memory cell, in which an active material (insulator) is sandwiched between two metal electrodes. Under external unipolar voltage (DC) and/or bipolar electric voltage (AC), the electrical resistance of active layer (insulator) can be switched from high resistance state (HRS), i.e. OFF state to low resistance state (LRS), i.e. ON state and vice versa. The switching of the device from LRS→ HRS→LRS→HRS→ $\cdots$ continues under repeated cycles of externally applied voltage. The device remembers its last resistance state. If we designate logic 0 to HRS and logic 1 to LRS, the data get stored in the binary form and leads to the formation of memory device. Although the resistive switching has been extensively studied for various metal oxides like NiO, $SrTiO_3$, ZrO_2, HfO_2 and oxides of spinel ferrites, the highly efficient active material is yet to be investigated for high quality resistive switching having negligible fluctuations in HRS as well as in LRS. Other switching parameters like retention, endurance, ON/OFF ratio must be excellent for commercial applications of memory device. As ferrite materials show remarkable electrical, magnetic, physiochemical, physiomechanical and optoelectronic properties, scientists have started to investigate resistive switching (RS) in ferrites like $NiFe_2O_4$, $ZnFe_2O_4$ and $CoFe_2O_4$ [3,4,6]. To fulfil the commercial demand for RS memory cell, various mixed ferrites have been synthesised and characterised for resistive switching applications. Some of the mixed ferrites, which have been employed as active materials for resistive switching are nikel zinc ferrite, Cu-doped nickel ferrite, Cu-doped zinc ferrite, Cd-doped cobalt ferrite etc. [7–12]. As cobalt ferrite is a good insulator as well as highly stable towards thermal effect, attempts are made to enhance the RS quality

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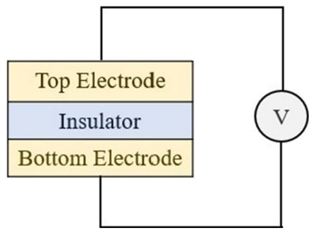

Figure 1. MIM Configuration.

in $CoFe_2O_4$ (CFO) by various means. Therefore, this review article on $CoFe_2O_4$ (CFO) as an active material is being communicated.

2. Operation of the memory cell

The nature of the top and bottom electrode materials in the metal/insulator/metal (M/I/M) memory cell configuration plays a vital role during RS [13]. The perfect explanation for the origin of RS in M/I/M memory cell is controversial and requires more theoretical investigations [14]. In this context, extensive investigation on cobalt ferrite-based memory cell has been carried out and attempts are made to elucidate the concrete theory for the physical origin of RS switching in M/I/M memory cell. It has been observed that the RS mode of cobalt ferrite as an insulator in M/I/M memory configuration is either unipolar or bipolar [15–21]. In the unipolar resistive switching (URS) mode, the switching from one state to another state solely depends on the magnitude of the externally applied electric potential as shown in figure 2.

Hence, SET and RESET can be achieved during the same polarity of applied voltage. On the other hand, in bipolar resistive switching (BRS), the transition of active material from one resistance state to another is characterised by the polarity of externally applied electric potential as shown in figure 3.

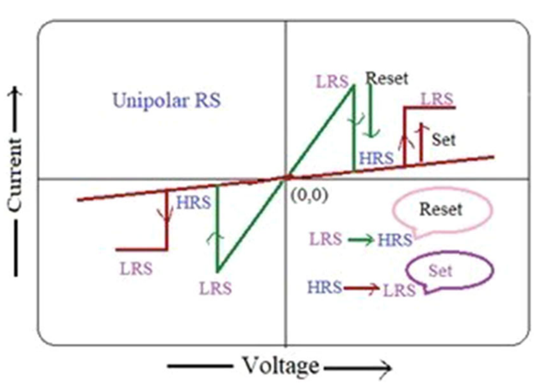

Figure 2. Unipolar resistive switching cycle.

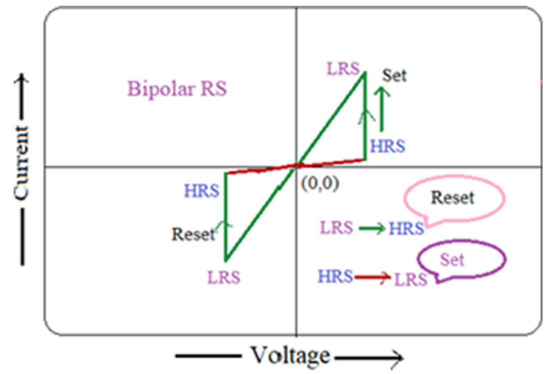

Figure 3. Bipolar resistive switching cycle.

In other words, BRS depends on the magnitude as well as the polarity of externally applied electric potential to the memory cell. Thus, SET and RESET switchings require opposite polarity of externally applied potential. Cobalt ferrite shows either unipolar resistive switching or bipolar resistive switching [22–24]. The entire process of unipolar and bipolar switching cycles is clearly explained in figures 2 and 3 respectively. The metal/insulator/metal (M/I/M) configurations of CFO-based RRAM devices and associated operational parameters are tabulated in table1. Herein, we have considered the RS parameters such as

- Resistance ratio: It is the ratio of resistance of the high resistance state (HRS), R_{HRS}, to resistance of low resistance state (LRS), R_{LRS}. It is expressed as R_{HRS}/R_{LRS}. The minimum value of resistance ratio should be 10, to differentiate between LRS and HRS for resistive RAM applications. The greater the resistance ratio, higher is the data storage density.
- Endurance: It is the number of SET or RESET cycles that continue till the merging of HRS and LRS.
- Retention: It is the time duration for which the memory cell stays in one particular state (either HRS or LRS) after programming or erasing.
- Operating voltage: The programming and erasing voltages should be as low as possible for gaining potential advantages over flash memory.

From tables 1 and 2, we can conclude that Cu/CFO/Pt memory cell has potential advantages over other metal/insulator/metal memory devices, as far as overall switching characteristics are considered. It has a good resistance ratio of $>10^4$, highest endurance of >500 and good retention time of more than 10^5 s. Comparatively, the power consumption is the lowest for Cu/CFO/Pt memory device as the values of readout voltage and operating voltage are smaller. Additionally, it shows BRS within 100 nm thick layer of CFO. This shows future scope for the Cu/CFO/Pt memory cell in the

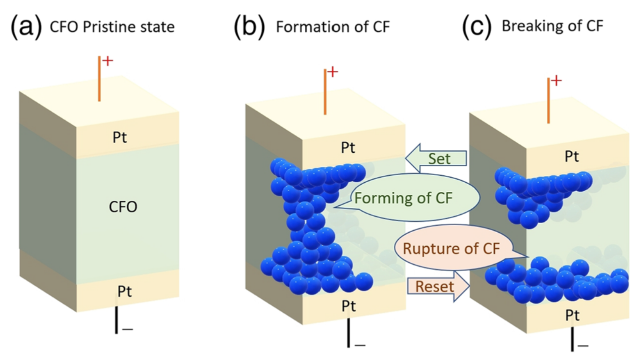

Figure 4. Formation and breaking of the conducting filament.

miniaturisation of the RRAM cell. Equally competent memory cell is Pt/CFO/Nb:$SrTiO_3$. The active material CFO thin film was synthesised using pulsed laser deposition (PLD) technique. It shows the highest resistance ratio of 5×10^5 and good range of operating voltage. The memory cell Pt/CFO/Nb:$SrTiO_3$ was found to be forming free (FF) and hence it consumes comparatively less electric energy. Therefore, power consumption is less. But, the values of endurance and retention for Pt/CFO/Nb:$SrTiO_3$ were observed to be comparatively lower. From table 2, we can infer that the nature of the electrode material influences the resistive swiching mode. The electrochemical response of the top and bottom electrode materials influences the RS mode.

2.1 *Unipolar resistive switching*

The unipolar resistive switching has been observed in Pt/$CoFe_2O_4$/Pt memory cell [4]. Many theoretical models have been proposed to explain the physical origin of RS [5]. However, RS of the Pt/$CoFe_2O_4$/Pt memory cell can be well understood by using the conducting filament (CF) model [4,21]. Figure 4 represents the mechanism of formation and breaking of the conducting filament by applying unipolar electric field.

As shown in figure 4a, the positive terminal of the battery is connected to the top electrode (Pt) whereas the negative terminal is connected to the bottom electrode (Pt). The SET/RESET processes can be understood as follows:

2.1.1 *Electroforming process/SET process.* An external unipolar electric voltage is applied to the two electrodes (top and bottom) of the memory device as shown in figure 4a. The insulating material in the device has its own microstructure with all types of migrated cations and anions at their respective crystallographic site, crystal defects, small and big polarons and even dislocations. These in turn induce oxygen vacancies or

Table 1. M/I/M configuration and resistive switching parameters.

Sr. No.	M/I/M configuration	R_{HRS}/R_{LRS}	Endurance cycles	Retention (s)	Readout voltage (V)	Operating voltage (V)	Ref.
1	Pt/CFO/Pt	10^2	>100	$> 10^4$	−0.20	−0.65 to +1.50	[4]
2	Ag/CFO/Pt	–	>200	–	–	−2.00 to +1.50	[16]
3	Pt/CFO/Nb:$SrTiO_3$	5×10^5	>80	$> 10^3$	0.30	+2.00 to −2.00	[20]
4	Cu/CFO/Pt	$>10^4$	>500	$>10^5$	0.10	−2.00 to +2.00	[27]
5	Al/CFO/FTO	10^3	200	10^4	0.10	+5.00 to −5.00	[28]

CFO: $CoFe_2O_4$; R_{HRS}: resistance of high resistance state; R_{LRS}: resistance of low resistance state.

Table 2. M/I/M configuration and resistive switching modes.

Sr. No.	M/I/M configuration	Active material	Synthesis technique of the active material	Active layer thickness (nm)	RS Mode	FF FR	V_F (V)	Ref.
1	Cu/CFO/Pt	CFO	–	100	BRS	FR	3.0	[27]
2	Pt/CFO/Pt	CFO	Sol–gel spin coating	120	URS	FR	4.2	[4]
3	Pt/CFO/Nb:$SrTiO_3$	CFO	Pulsed laser deposition	150	BRS	FF	Nil	[20]
4	Al/CFO/FTO	CFO	Sol–gel spin coating	200	BRS	FR	6.5	[28]
5	Ag/CFO/Pt	CFO	Spray pyrolysis	5600	BRS	–	–	[16]

CFO: $CoFe_2O_4$; FF: forming free and FR: forming required.

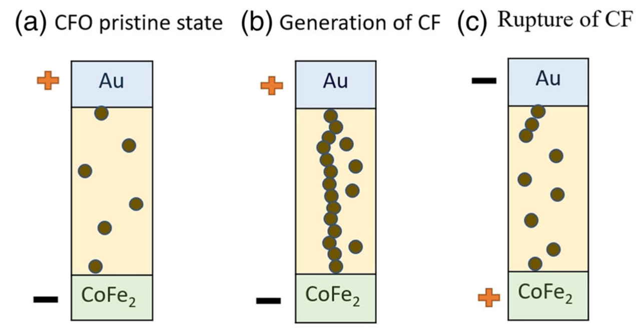

Figure 5. Bipolar resistive switching mechanism.

migrating metal ions. The blue spheres in figure 4b represent oxygen vacancies and/or metal ions. These oxygen vacancies and/or metal ions together generate CF. The CF grows across the insulator thin film. Thus, the growth of CF starts from the interface of the top electrode–insulator, extends through the active layer and ends at the interface of the insulator–bottom electrode as shown in figure 4b. The resistance of the memory cell reduces drastically. The memory cell is switched from HRS to LRS and hence remarkable current flows in the circuit. This is called the SET process or the electroforming process. The conduction mechanism in the LRS is governed by Ohm's Law.

2.1.2 *Rapturing of conductive filament/RESET process.* Once the memory device is switched to LRS, the charges flow through the conducting filament and hence electrical conduction occurs. Further increase in external potential generates joule heating around the filament and hence the filament breaks as shown in figure 4c. This is called the soft breakdown. The device switches to HRS. The switching of the memory cell from LRS to HRS is called the RESET. The conduction mechanism of HRS is dominated by Schottkey emission and Poole–Frenkel emission. The formation and rapture of the CF is demonstrated in figure 4.

2.2 *Bipolar resistive switching*

The Au/$CoFe_2O_4$/$CoFe_2$ memory cell exhibits bipolar resistive switching mechanism which can be understood as follows [19]:

2.2.1 *SET process.* When positive voltage is applied to the bottom as shown in figure 5a, the ionised oxygen vacancies migrate towards the bottom electrode and get settled at the interface between $CoFe_2O_4$ and the lower electrode. These oxygen vacancies capture the electrons released from the negative terminal of the applied voltage and transform Fe^{3+} ions to Fe^{2+}. Thus formed, Fe^{2+} and oxygen vacancies can form non-stoichiometric and highly conducting phase, which grows from $CoFe_2O_4$–bottom electrode interface and extends to the anode, i.e. positive terminal. By increasing the voltage, creation of conducting path between the anode and the cathode is expedited and the memory cell is switched to LRS as shown in figure 5b. This is equivalent to the stable ON state of a bistable multivibrator.

2.2.2 *RESET process.* The memory cell remains in the same state till the opposite polarity of the external voltage is applied. When opposite polarity voltage is applied, the neutral oxygen vacancies release the electrons and thus the conducting path dissolves and memory cell switches to HRS as shown in figure 5c.

2.3 *Forming-required (FR) and forming-free (FF) processes*

If the memory device requires application of an external electric voltage for the initialisation of switching process from HRS to LRS for the first time, the device is accompanied by forming-required process. The necessary external voltage is called the electroforming voltage which is denoted by V_F. Forming-free process occurs when the memory device switches from HRS to LRS for the first time without the help of operating voltage [21,25].

3. Result and discussion

The performance of the ferrite in resistive RAM depends on the synthesis route of the active material, its chemical composition, microstructure, material of the electrode used and even on stacking of the M/I/M sandwich. Hence, we have tabulated the results in tables 1 and 2. Table 1 compares the operational parameters of the resistive RAM by changing the electrodes with fixed active material. Table 2 compares the influence of synthesis route on the performance of the resistive RAM again fixing $CoFe_2O_4$ as the active material.

Cobalt ferrite as an active material for the RS application is significant for RRAM. The discussions on different results are critically reviewed and the inferences drawn from the review are listed as follows:

- Proper selection of the top and bottom electrodes is required to get excellent switching response. From the comparative study made in table 1, one can conclude that, $Pt/CoFe_2O_4/Nb{:}SrTiO_3$ heterostructure memory cell shows the highest resistance ratio, excellent endurance, good retention and forming-free switching cycles.
- Forming voltage increases with the thickness of the active material in spin-coated active material of the MIM structures.
- The material of the top and the bottom electrodes plays a vital role in resistive switching. The mode of the resistive switching depends on the nature of the electrode material.
- In memory devices, where the top and the bottom electrodes are made up of the same electrochemically active material, the resistive switching exhibits unipolar resistive switching (URS). But, memory devices, where the top and the bottom electrodes are of different kinds of materials, i.e., one of the electrode is electrochemically active like platinum (Pt) and the counterelectrode is silver (Ag), copper (Cu), or aluminium (Al), exhibit bipolar resistive switching.
- The resistive switching dependance on the nature of the top and bottom electrode materials is because of the activation energy, work function and the barrier height. Platinum (Pt) electrode has the lowest activation energy, which causes high probability of the generation/elimination of oxygen vacancies near the interface. This affects the electrical characteristics of the RS cycles. Thus, the activation energy of Cu and Al in M/I/M cells $Cu/CoFe_2O_4/Pt$ and $Al/CoFe_2O_4/FTO$ is responsible for distinct properties, though the active material is the same.
- Cobalt ferrite as an active material can be synthesised by many routes. Some of the synthesis techniques are: sol–gel synthesised spin coating, sputtering, molecular beam epitaxy, spray pyrolysis, ion beam deposition and pulsed laser deposition. However, pulsed laser deposition (PLD) technique is promising because its substrate temperature requirement is lower than the sol–gel process. Using PLD techniques, one can control the surface structure, particularly of the cobalt ferrite thin film, and hence tune the properties as per the requirement of resistive switching.
- The expected values of the resistive switching parameters are as follows: The endurance of the device as reported is as high as 10^6 cycles, the retention time is around 10 years and the operating speed of the device is as low as 10 ns. Forming-free memory device is ultimately a power saving device compared to the forming-required memory cell.

4. Conclusion

The aforementioned results and discussions made on the review of the literature survey shows that cobalt ferrite is undoubtedly an active material for application in RRAM. The reader develops a proper insight into the functioning of the memory cell device. Different necessary memory cell parameters are properly introduced and explained. The optimal parameters required are also mentioned in this review article.

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References

[1] B-H Lee, H Bae, H Seong, D-I Lee, H Park, Y J Choi, S-G Im, S O Kim and Y-K Choi, *ACS Nano*. **9**, 7306 (2015)
[2] R Chen, W Hu, A Hao and D Bao, *J. Mater. Sci.: Mater. Electron.* **30**, 21477 (2019)
[3] W Hu, N Qin, G Wu, Y Lin, S Li and D Bao, *J. Am. Chem. Soc*. **134**, 14658 (2012)
[4] W Hu, L Zou, R Chen, W Xie, X Chen, N Qin, S Li, G Yang and D Bao, *Appl. Phys. Let*t. **104**, 143502 (2014)
[5] Min Hwan Lee and Cheol Seong Hwang , *Nanoscale*. **3**, 490 (2011)
[6] M Ismail, A Hao, W Huang, J Lee, S Kim and D Bao, *Appl. Phys. Lett.* **113**, 152103 (2018)
[7] Lei Wu, Chunhui Dong, Xiaoqiang Wang, Jinsheng Li and Mingya Li, *J. Alloys Compd*. **779**, 794 (2019)
[8] D K Pradhan, S Kumari, L Li, R K Vasudevan, P T Das, V S Puli, D K Pradhan, A Kumar, P Misra, A K Pradhan, S V Kalinin and R S Katiyar, *J. Appl. Phys.* **122**, 033902 (2017)
[9] A Hao, D Jia, M Ismail, W Huang, R Chen and D Bao, *Appl. Phys. Lett*. **114**, 203502 (2019)
[10] Aize Hao, Dianzeng Jia, Muhammad Ismail, Ruqi Chen and Dinghua Bao, *J. Alloys Compd.* **790**, 70 (2019)
[11] Bai Sun, Xin Zhang, Guangdong Zhou, Chunming Zhang, Pingyuan Li, Yudong Xia and Yong Zhao, *J. Alloys Compd.* **694**, 464 (2017)
[12] U V Chhaya, B V Mistry, K H Bhavsar, M R Gadhavi, V K Lakhani, K B Modi and U S Joshi, *Indian J. Pure Appl. Phys*. **49**, 833 (2011)
[13] Ravi Prakash, Bhawani Pratap Singh Rathore and Davinder Kaur, *J. Alloys Compd*. **726**, 693 (2017)
[14] Jui-Yuan Chen, Cheng-Lun Hsin, Chun-Wei Huang, Chung-Hua Chiu, Yu-Ting Huang, Su-Jien Lin, Wen-Wei Wu and and Lih-Juann Chen, *Nano Lett*. **13**, 7671 (2013)
[15] S Slesazeck and T Mikolajick, *Nanotechnol*. **30**, 352003 (2019)
[16] T D Dongale, A A Bagade, S V Mohite, A D Rananavare, M K Orlowski, R K Kamat and K Y Rajpure, *J. Mater. Sci.: Mater. Electron.* **29**, 3231 (2018)
[17] C Jin, D X Zheng, P Li, W B Mi and H L Bai, *Appl. Surface Sci.* **263**, 678 (2012)
[18] M Kamran and M Anis-ur-Rehman, *J. Alloys Comp*. **822**, 153583 (2020)
[19] C Jiang, L Wu, W W Wei, C Dong and J Yao, *Nanoscale Res. Lett*. **9**, 584 (2014)
[20] Q Wang, Y Zhu, X Liu, M Zhao, M Wei, F Zhang, Y Zhang, B Sun and M Li, *Appl. Phys. Lett*. **107**, 063502 (2015)
[21] Millaty Mustaqima, Pilsun Yoo, Wei Huang, Bo Wha Lee and Chunli Liu, *Nano Express.* **10**, 168 (2015)
[22] R Chen, W Hu, L Zou, W Xie, B Li and D Bao, *Appl. Phys. Lett.* **104**, 242111 (2014)
[23] F Pan, S Gao, C Chen, C Song and F Zeng, *Mater. Sci. Eng. R* **83**, 1 (2014)
[24] T Kurosawa, Y C Lai, T Higashihara, M Ueda, C L Liu and W C Chen, *Macromolecules* **45**, 4556 (2012)
[25] Zedong Xu, Min Gao, Lina Yu, Liying Lu, Xiaoguang Xu and Yong Jiang, *ACS Appl. Mater. Interfaces* **6**, 17823 (2014)
[26] Li Ying Tao, Long Shi Bing, Liu Qi, Lu Hang Bing, Liu Su and Liu Ming, *Chin. Sci. Bull*. **56**, 3072 (2011)
[27] Sandeep Munjal and Neeraj Khare, *Appl. Phys. Lett*. **113**, 243501 (2018)
[28] Sandeep Munjal and Neeraj Khare, *Sci. Rep*. **7**, 12427 (2017)