

In-situ Observation of Resistive Switching Mechanism in SrCoO_x Based RRAM Device

Hung-Yang Lo¹, Guan-Min Huang¹, Ping-Hung Yeh² and Wen-Wei Wu^{1,*}

¹ National Chiao Tung University

Department of Materials Science and Engineering

No.1001, University Rd., East Dist., Hsinchu City 30010, Taiwan

Phone : +886-3-5712121#55395 E-mail: wwwu@mail.nctu.edu.tw

² Tamkang University

Department of Physics

No.151, Yingzhuan Rd., Tamsui Dist., New Taipei City 25137, Taiwan, R.O.C.

Phone : +886-2-2621-5656#2819

Abstract

Resistive random access memory (RRAM) has attracted considerable interest for next-generation non-volatile memory due to its fast switching speed, simple structure and scalability. To effectively control the switching characteristic with excellent memory performance, a complete study of the switching behavior is essential. In this work, we utilize SrCoO_x (SCO) which grows on Nb-doped SrTiO_3 (Nb-STO) substrate as our dielectric layer since it exhibits large different resistance between $\text{SrCoO}_{2.5}$ and $\text{SrCoO}_{3.6}$, where the value of $\text{SrCoO}_{2.5}$ is higher than that of $\text{SrCoO}_{3.6}$. Based on this characteristic, we fabricated a Au/SCO/Nb-STO device, and measured the SET (~ 1.6 V) and RESET (~ 5.3 V) process with more than 700 cycles. Meanwhile, the conducting filaments were observed via in-situ transmission electron microscope (TEM). From the HRTEM results and corresponding FFT-DP (Fast-Fourier-Transform Diffraction pattern), it is clearly demonstrated the formation of conducting filaments is from $\text{SrCoO}_{2.5}$ to $\text{SrCoO}_{3.6}$. Accordingly, the formation/rupture of conducting path is due to the movement of oxygen vacancy, and hence its resistance is able to switch reversibly between low resistance state and high resistance state. This study not only firstly revealed the switching mechanism of SrCoO_x but also proved it to be the promising candidate for RRAM application.

1. Introduction

Recently, resistive random access memory (RRAM) has attracted considerable interest for next-generation non-volatile memory due to its fast switching speed, simple structure and scalability.[1, 2] According to previous literature,[3, 4] the switching phenomena of conducting bridge RRAM is based on the conducting filaments (CF) theory. And the formation of CF could be distinguished between valence change mechanism (VCM) and electrochemical metallization mechanism (ECM).[5]

In this study, we utilize SrCoO_x (SCO) which grows on Nb-doped SrTiO_3 (0.5wt%Nb-STO) substrate as our dielectric layer since it exhibits large different resistance

between $\text{SrCoO}_{2.5}$ and $\text{SrCoO}_{3.6}$, where the resistance of $\text{SrCoO}_{2.5}$ is higher than that of $\text{SrCoO}_{3.6}$. [6] Moreover, in the previous literature, when apply the positive voltage, it could partially increase the oxygen pressure on $\text{SrCoO}_{2.5}$ then transform to $\text{SrCoO}_{3.6}$. [7] Based on this characteristic, we fabricated a Au/SCO/Nb-STO device, and measured the SET (~ 1.6 V) and RESET (~ 5.3 V) process with more than 700 cycles. Meanwhile, the conducting filaments were observed via in-situ transmission electron microscope (TEM). From the HRTEM results and corresponding FFT-DP (Fast-Fourier-Transform Diffraction pattern), it is clearly demonstrated the formation of conducting filaments is from $\text{SrCoO}_{2.5}$ to $\text{SrCoO}_{3.6}$. Accordingly, the formation/rupture of conducting path is due to the movement of oxygen vacancy, and hence its resistance is able to switch reversibly between low resistance state and high resistance state.

2. Methods, Results and Discussion

Methods

The asymmetric strontium cobaltite oxide-based RRAM, Au/ SrCoO_x /Nb-STO, was prepared. The SCO is deposited on Nb-doped STO substrate with PLD using a KrF excimer laser at substrate temperature of 650 °C, a pressure of 100 mTorr. Au pure metal was deposited by Electron Beam Evaporation. TEM sample was prepared by Focus Ion Beam, and then transferred on the electrifying chip, which was mounted on an in-situ TEM holder (Protochips Aduro300). The TEM we observe the reaction is JOEL F200.

Results and Discussion

Figure 1a shows the cross section of the sample, the SCO dielectric layer thickness is about 25 nm, the Au top electrode thickness is about 50nm, they are well-contacted between each layer. Figure 1b is HR-TEM image of SCO, and according to the FFT-DP, there is no crystalline structure in initial state of SCO. Then we applied the positive bias on the Au top electrode and negative bias on our Nb-STO substrate in atmosphere environments.

After applied the bias, in Figure 2a, we observe that the device exhibit the bipolar switching characteristic. The pristine resistance of device is high, as the bias apply to 12.6V,

the current suddenly reach the compliance current, we call this Forming. The CF is established as long as the Forming process complete, so the device doesn't require such high voltage to 'Set' (0.8V) the device to LRS. After the Forming or Set processes, we 'Reset' (-4V~-5.5V) the device to HRS. Moreover, the device can switch between LRS and HRS more than 700 cycles. The retention times measurement of our device is shown in Figure 2b, which could verify the CF stability. The retention time is more than 10^4 s and the read voltage is 0.2V. And Figure 2c shows the cumulative probability of Set and Reset voltage; the Set voltage range from 0.7V to 1.2V, and Reset voltage range from -4V to -5.7V. Figure 2d shows the cumulative probability of resistance in Au/SCO/Nb-STO device. The device ON/OFF ratio is about 10^3 , therefore, the device has large different resistance between LRS and HRS, indicating that SCO is an excellent RRAM material. Based on series electrical measurements, the SCO RRAM device shows the high endurance, great stability, and excellent retention times.

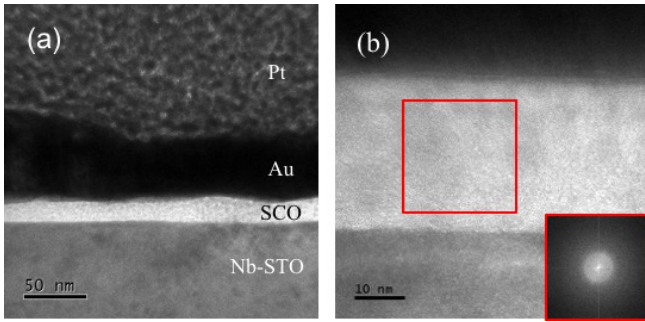


Fig. 1 TEM image of device before electrical measurement.

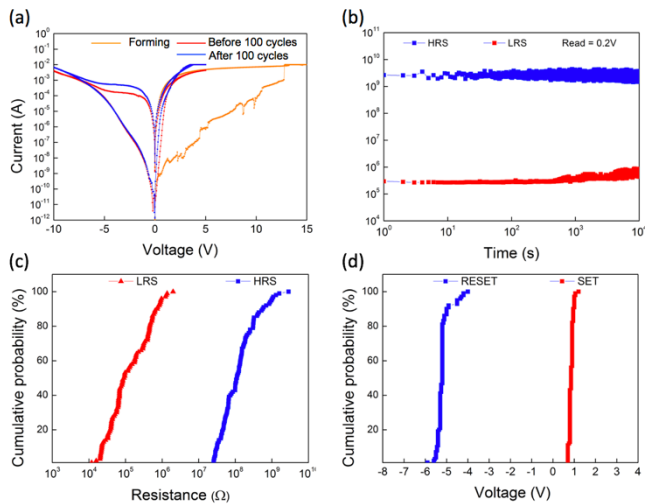


Fig. 2 RRAM Electrical properties of device

From the results of Figure 2, a series of switching characteristic in atmosphere, we want to know the switching mechanism of device, therefore, we utilize TEM to observe the change of microstructure after applied voltage on device.

In Figure 3a, after applying positive voltage, we observe the dark contrast area in SCO dielectric layer, and according to the FFT-DP, it is composed of SrCoO_3 . This phase transformation is mainly caused by the movement of oxygen vacancies. Meanwhile, when the negative bias is applied on the device, the resistance state of the device is back to HRS. In Figure 3b, TEM image shows that that dielectric layer is transformed to $\text{SrCoO}_{2.5}$, and the device is in HRS. The oxygen vacancies have moved toward the dielectric layer due to the electric field, which increase the oxygen vacancies in SCO, and make it transform to $\text{SrCoO}_{2.5}$.

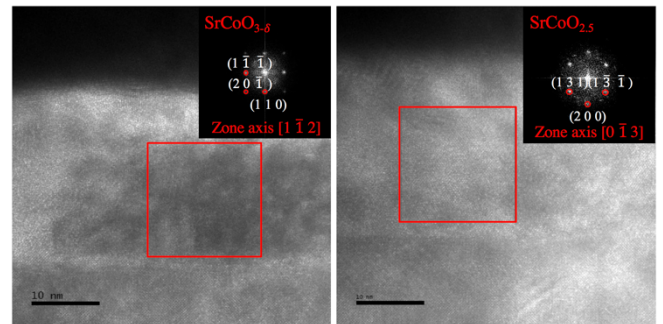


Fig. 3 HR-TEM image of device after electrical measurement.

3. Conclusions

In summary, the asymmetric Au/ $\text{SrCoO}_{2.5}$ /Nb-STO RRAM device not only has bipolar switching characteristic but also exhibits the highly durable and excellent stability. The electrical measurement show that the ON/OFF ratio is up to 10^3 , the Set and Reset voltage have narrow distribution, and the retention time can reach more than 10^4 s. Through the HR-TEM image, we observe that the CF formation and rupture is due to the movement of oxygen ions, which result in the phase transformation of SCO. The above results make SCO be the potential candidate of RRAM material.

Acknowledgements

We thank Prof. Ying-Hao Chu's group for fabricating SCO thin film via PLD system.

References

- [1] J.J. Yang, D.B. Strukov, D.R. Stewart, Nature Nanotechnology 8 (2012) 13.
- [2] T. Ohno, S. Samukawa, 106(17) (2015) 173110.
- [3] A. Sawa, Materials Today 11(6) (2008) 28-36.
- [4] R. Waser, R. Dittmann, G. Staikov, K. Szot, 21(25-26) (2009) 2632-2663.
- [5] C.-F. Chang, J.-Y. Chen, C.-W. Huang, C.-H. Chiu, T.-Y. Lin, P.-H. Yeh, W.-W. Wu, 13(15) (2017) 1603116.
- [6] H. Jeon, W.S. Choi, M.D. Biegalski, C.M. Folkman, I.C. Tung, D.D. Fong, J.W. Freeland, D. Shin, H. Ohta, M.F. Chisholm, H.N. Lee, Nature Materials 12 (2013) 1057.
- [7] Q. Lu, B. Yildiz, Nano Letters 16(2) (2016) 1186-1193.