

Characterization and analysis of thin film of Ruthenium complex (II) for Resistive Memory applications

S. KAUSHIK^{1,*}, S. PANDEY¹, R. SINGHAL²

¹Amity School of Engineering and Technology, Amity University Uttar Pradesh, Noida, India

²Malviya National Institute of Technology, Jaipur, India

The industry is looking at resistive memory devices, notably those based on solution-processable, chemically changeable organic materials that are low-cost. In this paper, we have fabricated Resistive Memory devices by spin coating a Ruthenium (II) thin layer which is organic in nature on an ITO substrate. The fabricated Resistive Memory devices, utilizing a Ruthenium (II) thin layer deposited on an ITO substrate via spin coating, exhibit low resistance and high resistance conduction states. These properties make them highly suitable for Resistive Random-Access Memory (RRAM) applications. RRAM has emerged as a promising non-volatile memory technology due to its high scalability, fast switching speed, and low power consumption. By utilizing the low and high resistance states, the Resistive Memory devices can effectively store binary data, offering potential applications in various memory-based systems, including solid-state drives, embedded systems, and Internet of Things (IoT) devices. The use of organic Ruthenium (II) thin layers presents a novel avenue for exploring the performance and stability of Resistive Memory devices, paving the way for further advancements in RRAM technology." Scanning electron microscope (SEM), X-ray diffraction (XRD), and Energy-dispersive X-ray spectroscopy (EDX) were used to characterise the device. Current-Voltage characteristics of these devices were also obtained. Low resistance and high resistance conduction states were measured and found perfect for Resistive random-access memory applications. Furthermore, we observe that with the increase in the thickness of the organic layer, the switching improves, and as a result, the resistance ratio improves by the ratio of 10.

(Received December 19, 2022; accepted August 7, 2023)

Keywords: Ruthenium, Switching, Devices, Electrical properties

1. Introduction

The area of resistive memory devices has advanced rapidly since Williams and Strukov's initial work in 2008, and the commercial viability of applications in next-generation computing, such as neuromorphic architectures, is currently being researched. [1] A diverse section of materials, including two-dimensional materials, inorganic oxides [2-8], polymers, and other molecular systems, have been examined as active components of resistive devices. [9-13].

A lot of research has been done on the Ruthenium complex in the last several years for several applications for devices. Ruthenium complexes are well-known as attractive options for, low-voltage devices, and high-efficiency including light-emitting diodes (LEDs) and dye-sensitized solar cells (DSSCs) [14-17]. Apart from that, ruthenium compounds could be used in organic bistable memory applications. Only non-ionic and a few ionic substances have been shown to have good bistable memory. Though high formation (voltage/current) and huge (set/reset) voltage remain obstacles in realising high-density memory, oxide devices have emerged as the most favourable choices in terms of application. Organic devices, among other things, have piqued the interest of researchers due to their solution processability and chemically tunable functions. In fact, certain organic devices made advances into display technology, while

others appear to be appealing for new applications such as flexible electronics [18-19]. The general commercialization of organic devices has been bad, and the resistive memory domain represents too many of these scenarios when compared to the significant scientific effort spent to it [20-21]. Insufficient stability, repeatability, low switching speed, endurance, and scalability cause difficulties. Systematic statistical study of device properties is required to address the issue of reproducibility, but this has seldom been demonstrated for organic resistive memory systems. As a result, creating an ionic coordination complex with an organic bistable memory application is difficult. In this paper, a novel MIM structure was produced by spin coating Hexamethyl benzene Ruthenium on ITO which shows the ideal condition of RRAM which is required for switching. I-V characteristics of the devices were evaluated via pressure contact. SEM, XRD, and EDX were used to characterise the device. High resistance and Low resistance conduction states are visible in I-V characteristics, which is appropriate for RRAM applications. Increasing the amount of molecular compounds also improves switching, resulting in a better resistance ratio.

2. Methods and materials

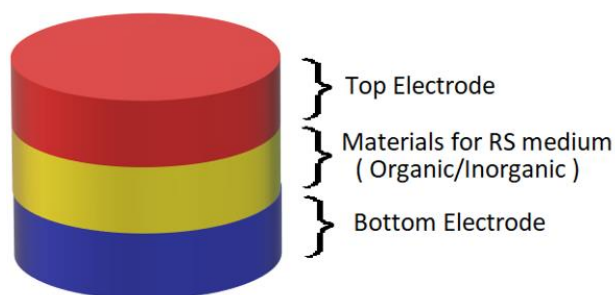


Fig. 1. Shows the basic Structure of RRAM (color online)

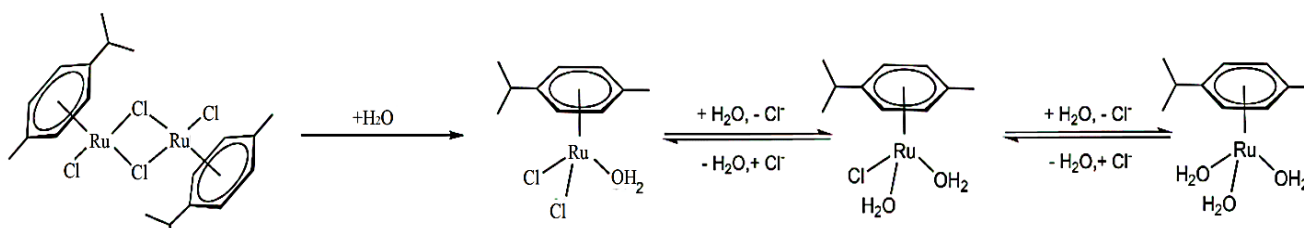


Fig. 2. Dimeric Ruthenium complex hydrolysis in water

Hydrolysis of dimeric Ruthenium complex in water gives a mixture of aqua complexes with the dicationic tri aqua being the major product [22]. The device structure

was ITO/Ruthenium/W (working electrode) as shown in Fig. 3.

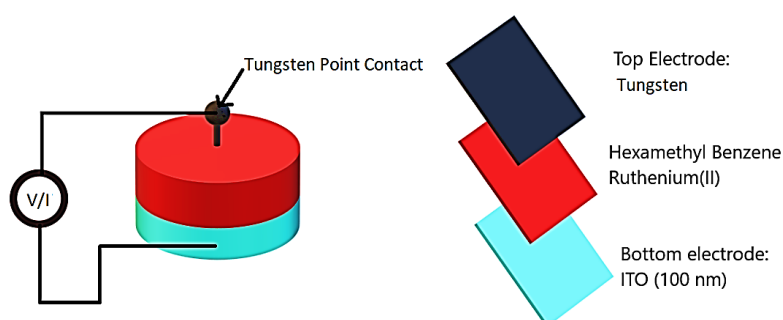


Fig. 3. Schematic of molecular film sandwiched between two electrodes (color online)

II. Device Characterization:

XRD characterizations

Fig. 4 below shows the X-ray diffraction (XRD) pattern of Ru (II) related to the expansion due to acetonitrile.

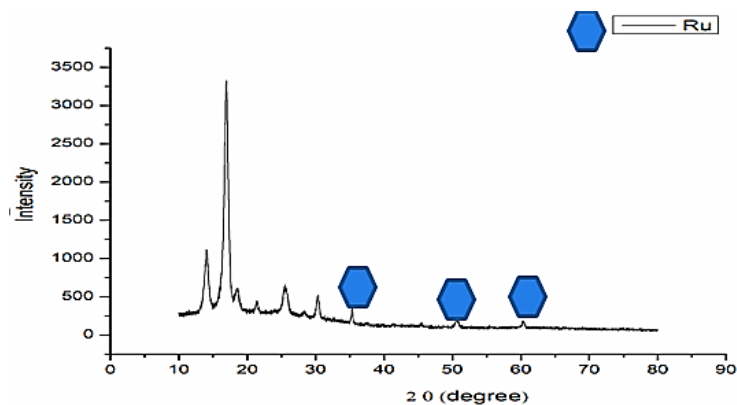


Fig. 4. XRD of high selectivity hydrogenation pattern of Ruthenium, Ru (II)

Ruthenium nanoparticles demonstrate high selectivity XRD patterns of catalyst activity prepared by reducing Ru (II) in water. As this catalyst activity is dependent on hydrogenation with acetonitrile, clusters of Hexamethylbenzene formation of Ru (II) nanoparticles [23] suggest that an aromatic π cloud can act as an H-bond. The carbon and oxygen atoms would likely coordinate to the Ruthenium surface and in turn receive the hydrogen atom already present at the surface of the Ru (II) nanoparticles.

3. SEM morphological characterization

The surface morphological features of the Ru (II) complex on the ITO sample are illustrated in the 200 nm SEM micrograph shown in Fig. 5. SEM micrograph shows Ru (II) synthesized complex leads to zigzag aligned nanorods. Moreover, the thorough distribution of these nanorods in the synthesized Ru (II) complex nanoparticles is further determined by energy-dispersive X-ray spectroscopy (EDX) measurement Fig. 6. The distribution of elements O, Si, In, C, Ru, Ca, Na, Al, and Mg can be seen successfully as also reported previously [24]. In

addition, elemental analysis from EDX spectrum is verified in Fig. 6 found to be O, 28.04%; Si, 20.84%; In, 18.80%; C, 18.08%; Ru, 5.14%; Ca, 3.64%; Na, 3.20%; Al, 1.34%; and Mg, 0.92%.

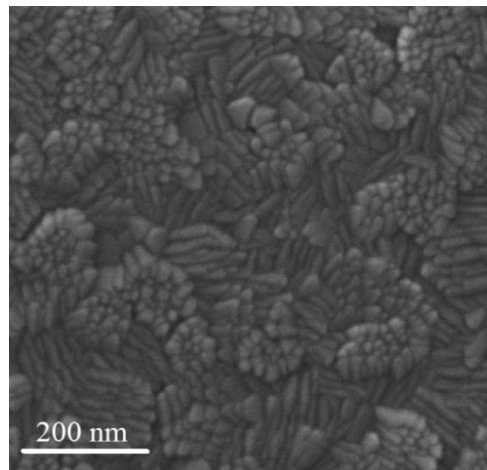


Fig. 5. Ru (II) nanoparticle synthesis SEM micrograph image

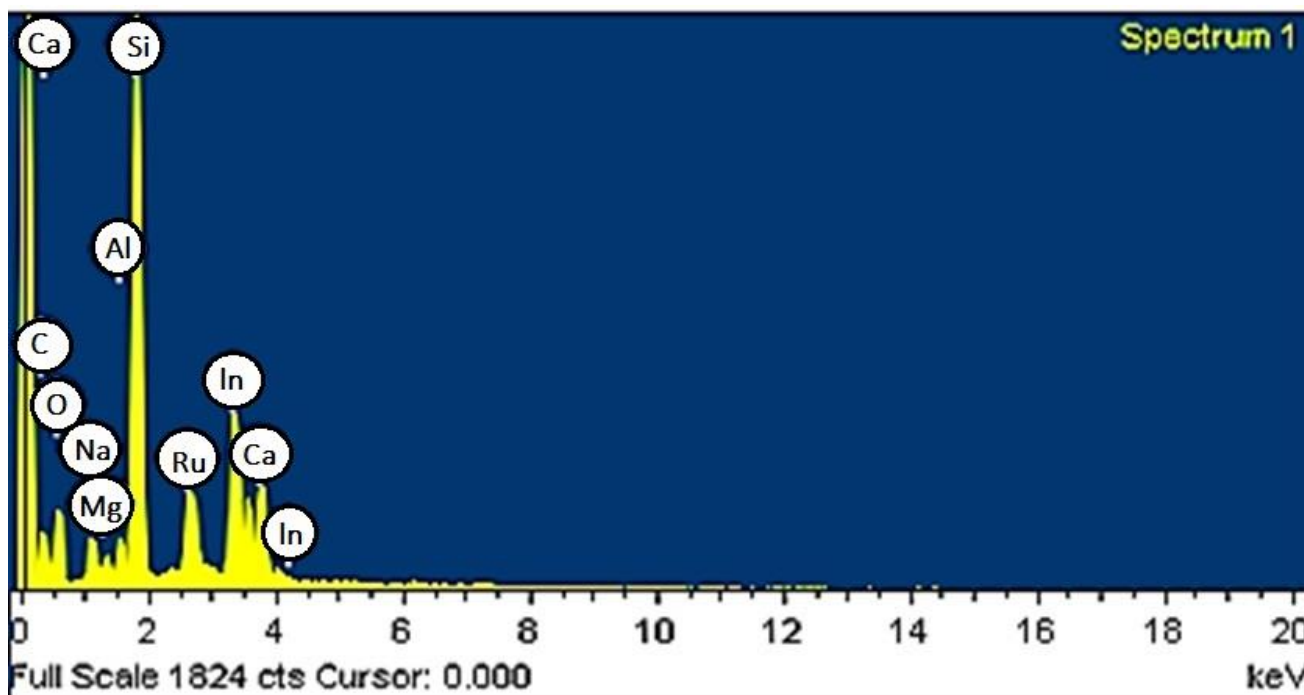


Fig. 6. EDX spectrum of Ruthenium, Ru (II) complex showing various elements (color online)

4. Results and discussion

Switching characteristics

I-V Characteristics determined and provide low resistance and high resistance states, which are appropriate for RRAM applications. The I-V measurement is carried out. Using a two-probe probe station with a Keithley

6517b electrometer and a pressure contact electrode constructed of W metal. To get the I-V characteristics, the voltage at the top electrode varies from -0.3 to +0.3 V. In Fig. 7(a), (b) and (c) the switching characteristics showed hysteresis. We also found that as the amount of Ruthenium increases, we get a better switching ratio. A high ratio of 10, particularly at ambient temperature and low voltage (0.3V) and in single-layer sandwich architectures, is

intriguing in and of itself. This is owing to the Ruthenium's electron-accepting nature and the complex's low OFF-state leakage current.

I-V characteristics are very much encouraging, as a result, Ruthenium can be used for RRAM applications.

5. Conclusion

The I-V properties of a Ruthenium (II) thin film produced by pressure contact spin coating on an ITO substrate, which displayed low resistance and high resistance conduction states, which is appropriate for RRAM applications, are described in this paper. It also demonstrates that when the amount of molecular components grows, so does the switching, and we get a better resistance ratio. The current study shows the applicability of Ruthenium complexes for RRAM applications.

Acknowledgement

We are obliged to Dr Saif A. Khan and Mr. Ramcharan Meena for helping in SEM and I-V measurements. Dr. Ranjit Kumar, who assisted in the creation of the sample and provided technical guidance and interesting ideas, is thanked by the author. The authors would like to express their gratitude to the Department of Science and Technology of the Government of India for funding this research through the WoS-A scheme (reference number SR/WOSA /ET-91/2018).

References

- [1] D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, *Nature* **453**, 80 (2008).
- [2] J. J. Yang, D. B. Strukov, D. R. Stewart, *Nat. Nanotech.* **8**, 13 (2013).
- [3] M. Prezioso, F. Merrikh-Bayat, B. D. Hoskins, G. C. Adam, K. K. Likharev, D. B. Strukov, *Nature* **521**(7550), 61 (2015).
- [4] K. M. Kim, J. J. Yang, J. P. Strachan, E. M. Grafals, N. Ge, N. D. Melendez, Z. Li, R. S. Williams, *Scientific Reports* **6**(1), 1 (2016).
- [5] A. Wedig, M. Luebben, D. Y. Cho, M. Moors, K. Skaja, V. Rana, T. Hasegawa, K. K. Adeplli, B. Yildiz, R. Waser, I. Valov, *Nature Nanotechnology* **11**(1), 67 (2016).
- [6] M. J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y. B. Kim, C. J. Kim, D. H. Seo, S. Seo, U. I. Chung, *Nature Materials* **10**(8), 625 (2011).
- [7] S. Kaushik, S. Pandey, R. Singhal, *ECS Journal of Solid State Science and Technology* **11**(3), 035003 (2022).
- [8] S. Kaushik, R. Singhal, D. K. Avasthi, **2020 IEEE International Conference on Electrical Engineering and Photonics (EExPolytech)** 22 (2020).
- [9] V. K. Sangwan, D. Jariwala, I. S. Kim, K. S. Chen, T. J. Marks, L. J. Lauhon, M. C. Hersam, *Nature Nanotechnology* **10**(5), 403 (2015).
- [10] M. Yoshida, R. Suzuki, Y. Zhang, M. Nakano, Y.

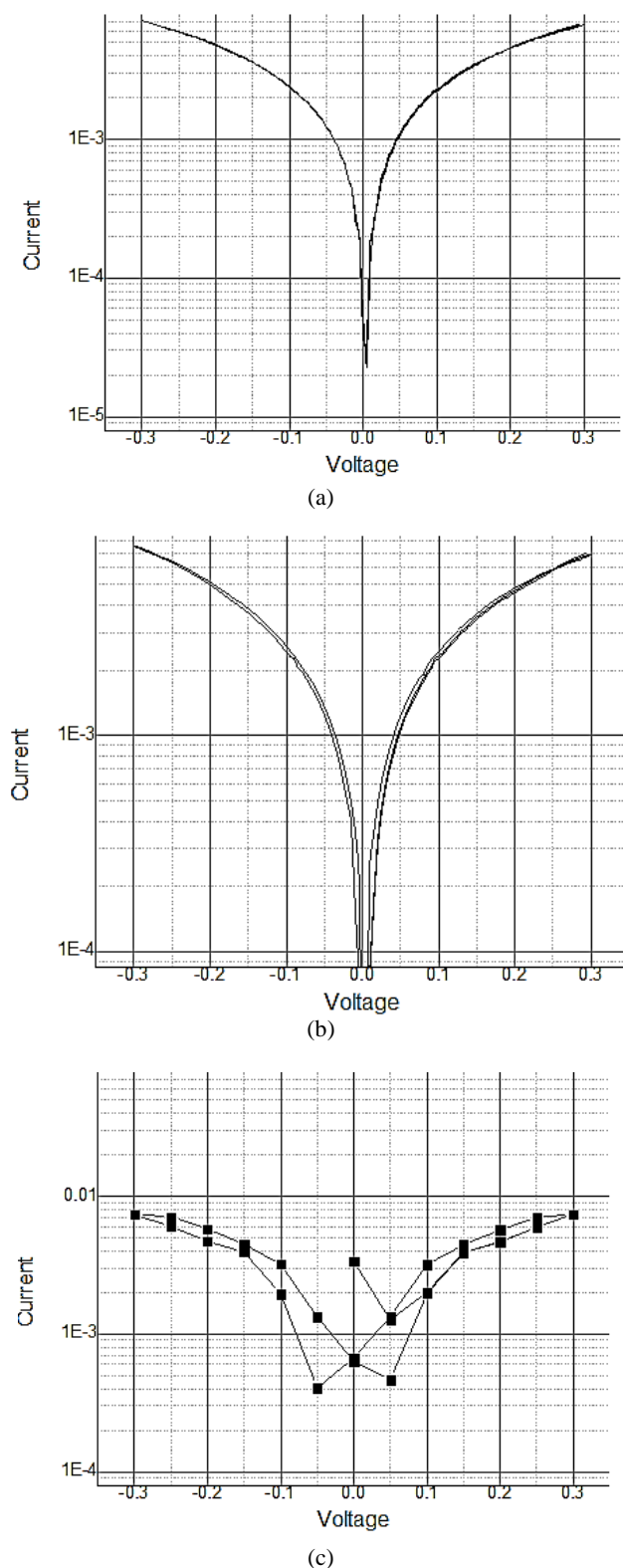


Fig. 7. I-V characteristics of the Ruthenium complex of various samples (a) Two drops of Ruthenium (b) Three drops of Ruthenium (c) Four drops of Ruthenium

- Iwasa, *Science Advances* **1**(9), e1500606 (2015).
- [11] W. P. Lin, S. J. Liu, T. Gong, Q. Zhao, W. Huang, *Advanced Materials* **26**(4), 570 (2014).
- [12] B. Hu, C. Wang, J. Wang, J. Gao, K. Wang, J. Wu, G. Zhang, W. Cheng, B. Venkateswarlu, M. Wang, P. S. Lee, *Chemical Science* **5**(9), 3404 (2014).
- [13] A. Bandyopadhyay, S. Sahu, M. Higuchi, *Journal of the American Chemical Society* **133**(5), 1168 (2011).
- [14] C. H. Lyons, E. D. Abbas, J. K. Lee, M. F. Rubner, *Journal of the American Chemical Society* **120**(46), 12100 (1998).
- [15] M. Buda, G. Kalyuzhny, A. J. Bard, *Journal of the American Chemical Society* **124**(21), 6090 (2002).
- [16] B. O'regan, M. Grätzel, *Nature* **353**(6346), 737 (1991).
- [17] J. Desilvestro, M. Graetzel, L. Kavan, J. Moser, J. Augustynski, *Journal of the American Chemical Society* **107**(10), 2988 (1985).
- [18] B. Cho, S. Song, Y. Ji, T. W. Kim, T. Lee, *Advanced Functional Materials* **21**(15), 2806 (2011).
- [19] M. Seal, A. Deogaonkar, A. Senapati, S. Maikap, N. Raghavan, *Microelectronics Reliability* **138**, 114623 (2022).
- [20] Shifeng Miao, Hua Li, Qingfeng Xu, Najun Li, Junwei Zheng, Ru Sun, Jianmei Lu, Chang Ming Li, *Journal of Materials Chemistry* **22**(32), 16582 (2012).
- [21] Shifeng Miao, Hua Li, Qingfeng Xu, Youyong Li, Shunjun Ji, Najun Li, Lihua Wang, Junwei Zheng, Jianmei Lu, *Advanced Materials* **24**(46), 6210 (2012).
- [22] Nanda D. Paul, Utpal Rana, Sreetosh Goswami, Tapan K. Mondal, Sreebrata Goswami, *Journal of the American Chemical Society* **134**(15), 6520 (2012).
- [23] Farooq-Ahmad Khan, Sana Yaqoob, Nourina Nasim, Yan Wang, Muhammad Usman, Anvarhusein A. Isab, Muhammad Altaf, Bing Sun, Islam H. El Azab, Hesham R. El-Seedi, *Catalysts* **11**(1), 66 (2021).
- [24] S. Kumar, P. Kumar, S. L. Jain, *RSC Advances* **3**(46), 24013 (2013).

*Corresponding author: 13shikhakaushik@gmail.com