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Resistive Switching Memory Properties of Electrodeposited Cu_2O Thin Films

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The Cu_2O thin film was developed using an electrodeposition approach for resistive memory application. The impact of the deposition voltage (1V, 2V, 3V, and 4V) on resistive switching (RS)/memristive properties of Cu_2O thin films was studied. The XRD spectrum reveals that deposited Cu_2O has a cubic crystal structure. The bipolar RS in $Al/Cu_2O/FTO$ device was clearly observed during the current-voltage (I-V) measurement. The basic memristive properties were calculated from I-V data. The charge transport studies suggested that the SCLC mechanism was responsible for device conduction, and RS was due to filamentary effect. The result suggested that the electrodeposition technique is useful to fabricate a memristive device for various applications.

Keywords: Electrodeposition, Cu_2O, Resistive switching; Memristor.

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1. INTRODUCTION

The resistive switching (RS) is an exciting phenomenon, owing to the reversible change in the resistive states of the device and therefore, can be used as a memory device. Additionally, the RS devices have a simple device configuration, making it a potential candidate for the crossbar memory application [1]. Moreover, the scalability and compatibility with the CMOS process are also a few benefits of RS devices [2]. Recently, memristive devices are extensively studied based on RS effect for various applications that include but not limited to the memory, sensor, logic and neuromorphic computing [3-4]. The RS devices are made up of two electrodes and sandwiched active switching layer. The external electric field forces a device for bistable resistance switching and to store the data in the form of the resistance.

In recent years, the RS devices are extensively developed and studied using solution-processable techniques. This is because the solution-processable techniques are inexpensive, simple, low-temperature process and scalable [5]. On the other hand, the physical deposition techniques such as atomic deposition techniques or sputtering are expensive and sophisticated. Given this, low cost and reliable memory devices are the need of the hour to carry out the necessary research and develop the end product. Among the many solution deposition techniques, the electrodepositio0n technique has multiple advantages. The electrodeposition method provides good film quality with large area deposition property which cannot be achieved by other techniques. The electrodeposition technique is cost-effective and takes a short time for uniform deposition of thin films as compared with other methods [6].

In the case of the electrodeposition, the cuprous oxide (Cu_2O) can be easily deposited on the conductive substrate. The Cu_2O is good semiconducting oxide materials with a direct bandgap [7].

Here, we have used the electrodeposition technique to deposited the Cu_2O on FTO and investigated the effect of the deposition voltage (1 V to 4 V) on the RS/memristive properties of Cu_2O thin films. In addition to this, we report the various memristive properties of the $Al/Cu_2O/FTO$ thin-film device. Moreover, the conduction mechanism was investigated and proposed the RS mechanism for the $Al/Cu_2O/FTO$ memristive device.

2. EXPERIMENTAL

The electrodeposition of the Cu_2O was carried out by using the two-electrode single-compartment electrochemical cell.The schematic illustration of the Cu_2O deposition is shown in Fig. 1a. The FTO substrate was used as a working electrode [8]. At the outset, the FTO substrate was treated with ultra-sonication to remove the dust and other surface impurities. Then it was cleaned using acetone, dysol, and iso-propanol for 20 min and finally rinsed with double distilled water. Two kinds of electrolyte solutions were used for the Cu_2O electrodeposition technique. The first electrolyte was the aqueous solution of 1M $CuSO_4.5H_2O$ and 6M sulphuric acid and the second electrolyte was the 4M sodium hydroxide (NaOH) dissolved in de-ionized water. Firstly, for the deposition of Cu, the Cu foil (anode) and FTO (cathode) were dipped into the first electrolyte and 1-4 V was applied between two electrodes. For further oxidation, Cu deposited FTO act as cathode whereas graphite rod as an anode, both were dipped in NaOH solution. Those of deposited film annealed in a furnace at a temperature of 200°C for 90 minutes. The electro-

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deposition voltage was changed from 1 V to 4 V to study the effect of deposition parameters on the RS properties of Cu_2O thin films. Aluminum (Al) top electrode was fabricated using a vacuum deposition technique. The typical device structure used in the present investigation is shown in Fig. 1b. The memristive properties of the Al/Cu_2O/FTO thin-film device were detected with the help of the ArC ONE instrument.

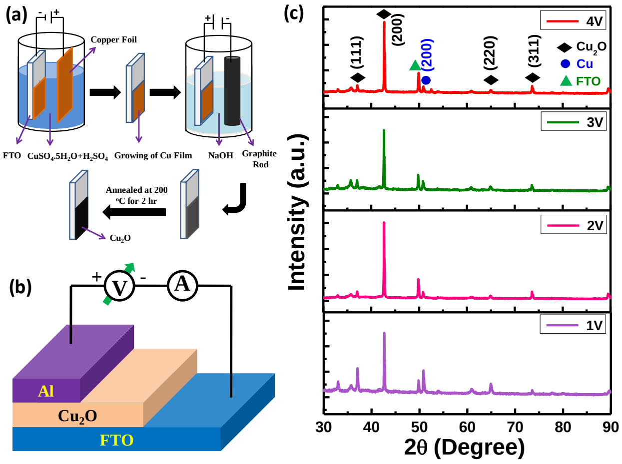

Fig. 1 – (a) schematic illustration of the Cu_2O deposition (b)device structure. (c)XRD spectra of Cu_2O thin films deposited at different voltages on the FTO substrate

3. RESULT AND DISCUSSION

The electrodeposited thin films were characterized using XRD (D2 phaser), as shown in Fig. 1c. The electrodeposition voltage-dependent XRD pattern suggested the presence of the significant peaks related to the Cu_2O. The XRD pattern shows that the intensity of the (200) crystal plane was higher as compared with the other planes. The existence sharp peaks at 37.20°, 42.72°, 64.97°, and 73.57° are correspond to (111), (200), (220), and (311)crystal planes, respectively. This data matches appropriately to the cubic Cu_2O structure (JCPDS No. 65-3288). In addition to this, a peak at 50.75° is corresponding to the (200) plane of the metallic Cu. It was observed that all deposited films show a cubic Cu_2O crystal structure. It was noticed that the intense peak of the (200) crystal plane grows with the deposition voltage. The crystallite size of deposited Cu_2O at 1, 2, 3, and 4V was found to be 10.88 nm, 10.61 nm, 11.36 nm, and 6.006 nm, respectively.

The developed Al/Cu_2O/FTO thin film devices were characterized using electrical measurements. The developed four devices were tested for I-V measurements (Fig. 2). The hysteresis loop was obtained for all Al/Cu_2O/FTO based devices, suggested the presence of memristive like property in the devices. In the present case, devices were tested in 0 V to ± 2V range, i.e., voltage bias was swept as $0V \rightarrow +2V \rightarrow 0V \rightarrow -2V \rightarrow 0V$. Initially, +5 V electroforming voltage was applied to the device for the proper operation. Initially, all devices are in the LRS, owing to the presence of a considerable number of oxygen vacancies and ions due to the electrodeposition process. These vacancies and ions could be distributed randomly in the active switching layer. The device switch to HRS, as the voltage reaches to the RESET voltage. It is observed that the RESET voltages tend to increases as the electrodeposition voltage increases. This is due to the fact that the higher electrodeposition voltage can form the thick film. Therefore, higher RESET voltage is needed to switch the device from one resistance state to another. However, the same SET voltage was required for all devices for RS operation, suggesting the SET voltage was independent of electrodeposition voltage. In the present case, the negative SET voltage switches the device from HRS to LRS. The nature of the hysteresis loop is found to be diverse for all Cu_2O based devices. In particular, negative differential resistance like *I-V* nature was noticed for the 1 V and 3 V deposited Cu_2O devices. This kind of negative differential resistance was also observed in some other memristive devices [9-10].

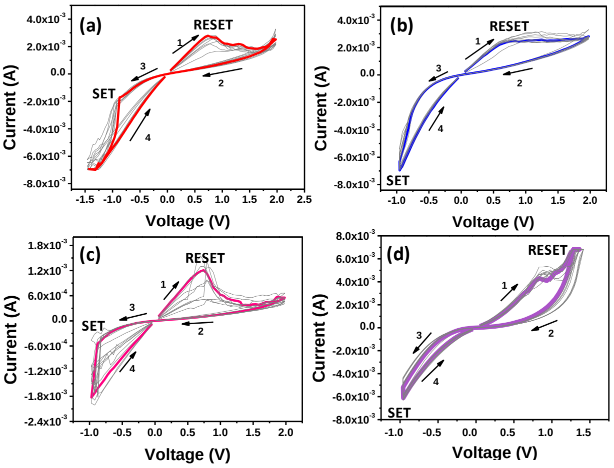

Fig. 2 – *I-V* curves of the Cu_2O based devices deposited at (a) 1V, (b) 2V, (c) 3V, (d) 4V. Arrows indicate the switching direction

The hysteresis loop observed in the Al/Cu_2O/FTO based devices suggested that the electrodeposited developed devices possess memristive like properties. In order to better understand the memristive nature of all devices, the flux and charge behavior was studied using experimental *I-V* data. The electrodeposition voltage-dependent (1 V to 4 V) time-domain flux, time-domain charge and charge-flux characteristic of the Al/Cu_2O/FTO thin film memristive devices are depicted in Fig. 3. In the present case, the asymmetric flux characteristic was observed for all Al/Cu_2O/FTO based memristive devices, as seen in Fig. 3a to d. This kind of asymmetric behavior is appeared due to the asymmetric values of switching voltages. Similarly, the asymmetric charge characteristic was observed for all Al/Cu_2O/FTO based memristive devices (Fig. 3e to h). The1 V and 2 V electrodeposited devices show negative charge values due to the active loop area under negative bias are higher than positive bias. The charge-flux properties of all devices demonstrated a double valued relation. This indicates that the Al/Cu_2O/FTO devices are non-ideal memristor devices or more Particularly they are memristive devices [11-12].The electronic conduction mechanism of developed devices can be understood by the fitting different charge transport mechanism to the obtained I-V data (Fig. 4). In the

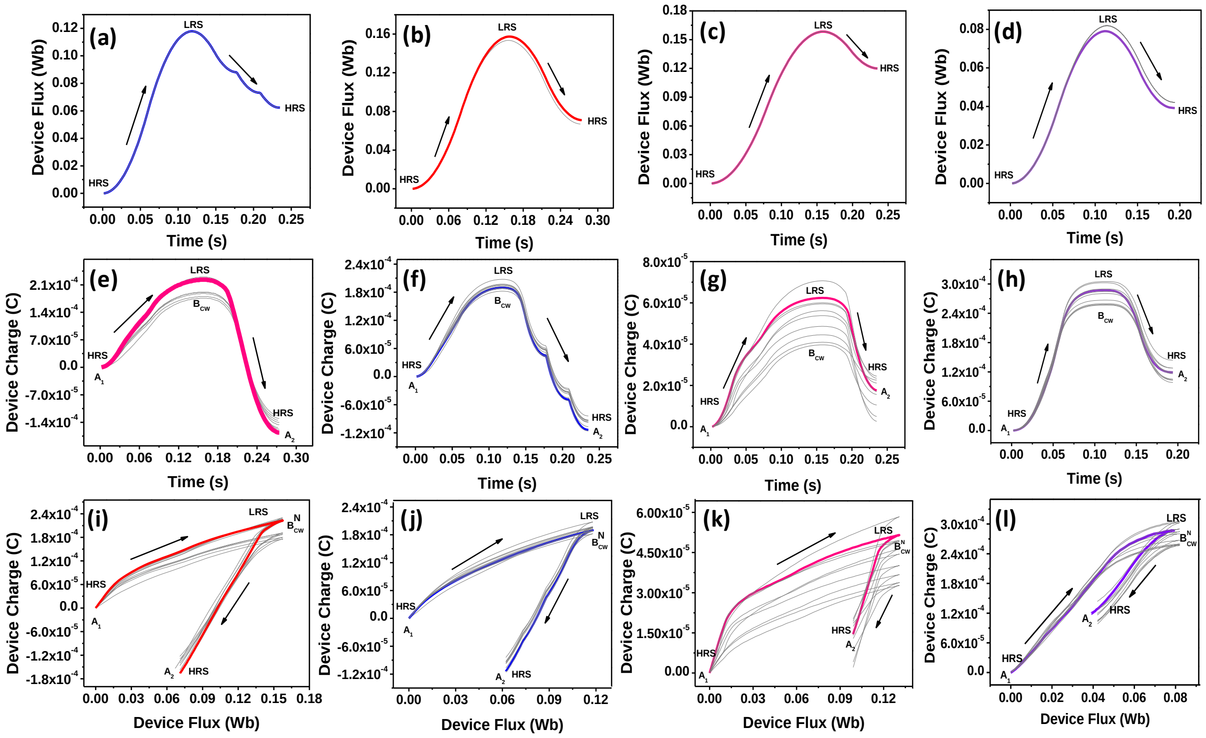

Fig. 3 – Electrodeposition voltage-dependent (1 V to 4 V) (a-d) time-domain flux, (e-h) time-domain charge and (i-l) charge-flux characteristic of the Al/Cu_2O/FTO memristive devices

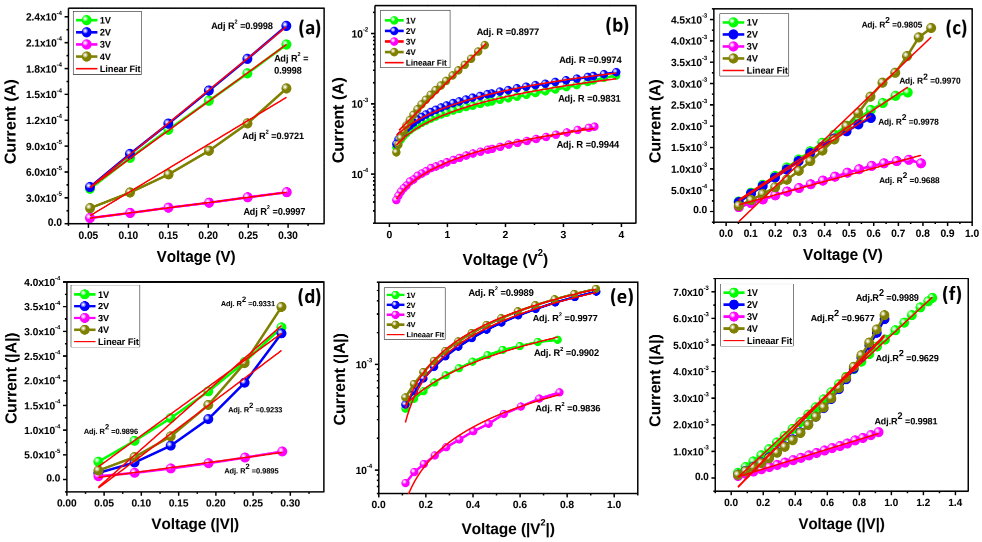

Fig. 4 – Electrodeposition voltage-dependent (1 V to 4 V) conduction mechanism fitting results of Al/Cu_2O/FTO memristive devices. Positive biased (a) low voltage region (HRS), (c) high voltage region (HRS)and (c) entire voltage region (LRS). Negative biased (d) low voltage region (HRS), (e) high voltage region (HRS) and (f) entire voltage region (LRS)

present case, HRS of all devices follows the Ohmic and child's square law at low and high voltage regions, respectively for both bias conditions. Alternatively, the LRS I-V data were well fitted with the Ohmic conduction model. The Ohmic and Child's square law fitting results of HRS suggested that SCLC was dominated in the HRS [13]. The electrical result reveals that the developed memristive devices show the bipolar RS characteristics with initial LRS. The initial LRS was observed due to a large number of defects present in the thin film during the deposition process.

The RS mechanism of the memristive devices is depicted in Fig. 5. The electrodeposited Cu_2O thin film has inherent oxygen vacancies and ions. These oxygen vacancies and ions play a remarkable role in the RS process by developing the conductive filament in the active switching layer. Initially, oxygen vacancies and ions were randomly distributed in the active switching layer, as shown in Fig. 5a. The electroforming process forces the oxygen vacancies and ions to forms the weak conductive filament. This weak conductive filament is responsible for the initial LRS instead of the HRS. Appling positive and negative voltage to the top and bottom electrode respectively, the oxygen vacancies moved towards the bottom electrode, and oxygen ions drift towards the top electrode, as shown in Fig. 5b. The oxygen vacancies and ions based conductive filament start to grow and current increases in the device with respect to the increase in positive voltage on the top electrode. At the RESET voltage, the Joule heating process was dominated, results in the breaking of the conductive filament, as shown in Fig. 5c.

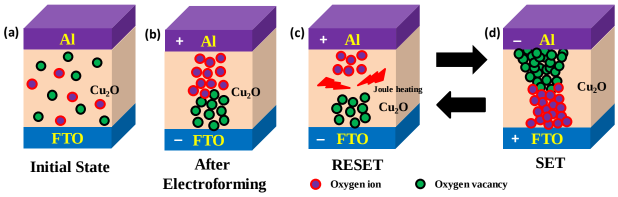

Fig. 5 – Possible RS mechanism of Al/Cu2O/FTO memristive device. (a) Initial state, (b) device after electroforming process, (c) RESET and (d) the SET process of the memristive device

Accordingly, the RESET voltage forces the device into HRS due to the Joule heating. As the polarity of the signal changes, the oxygen vacancies move towards the top electrode and ions drift towards the bottom electrode, as shown in Fig. 5d. This process leads to form the highly-dense conductive filament and the device again switches to the LRS. Given this, the alternating polarity reversal can switch the device in two resistance states and therefore, bipolar RS was observed in the developed devices.

4. CONCLUSION

An electrodeposition approach was used to develop the Cu_2O memristive devices and demonstrated the bipolar RS characteristics. The XRD data of all thin films are well matches with the cubic Cu_2O structure (JCPDS No. 65-3288). The average crystallite size of deposited Cu_2O at 1, 2, 3, and 4 V was found to be 10.88 nm, 10.61 nm, 11.36 nm, and 6.006 nm, respectively. All devices show the bipolar RS operation. It is observed that the magnitude of the RESET voltages depends on the electrodeposition voltage whereas; SET voltage is independent of electrodeposition voltage. The negative differential resistance like *I-V* nature was observed for 1 V and 3 V deposited Cu_2O devices. The charge-flux characteristic of all Al/Cu_2O/FTO memristive devices demonstrated the double valued relation. The analysis of electrical results suggested that the Ohmic and SCLC are responsible for device conduction and the filamentary mechanism was responsible for the bipolar RS.

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