Fabrication and Study of Memory Cell Switching Properties based on Ag_2S Compound

Azam Adnan Mohammed Al-Kubaa
PhD Student
University of Mosul
College of Engineering, Electrical Engineering Dept
Mosul, Iraq

Khalid Khaleel Mohammad, PhD
University of Mosul
College of Engineering, Electrical Engineering Dept
Mosul, Iraq

ABSTRACT
There are many materials having non-volatile resistance change has been studied as potential candidates for next generation of non-volatile memory devices, in this device, information is stored as a change in resistance due to the formation of the metallic filament via the reduction of metal ions in the solid electrolyte. Key attributes are low voltage, low current, rapid write and erase, good retention and endurance, and the ability for the storage cells to be physically scaled to a few nm. This paper presents experimental I-V characteristics and switching time results for solid state devices based on silver sulfide (Ag_2S) as new generation of non-volatile memory.

Keywords
Ag_2S memory cell, CBRAM, RRAM, ionic memory, non-volatile memory.

1. INTRODUCTION
Physical size reduction of memory based on charge storage (floating gate device) will result in unacceptable retention or state detection characteristics and the voltage, power, and cost requirements of upcoming memory applications, especially those in portable or "unconnected" systems, make many other approaches to solid state data storage undesirable [1]. Non-volatile memories based on phase transformation, reversible defect generation/recombination, filament and metallic Nano-wire growth/etch are being extensively studied as an alternative to floating gate based flash memory devices currently in use in stick memories and other applications [2]. One of the promising technologies under development for next generation non-volatile memory is the Conductive Bridging Random Access Memory (CBRAM) which utilizes the reversible switching of an electro resistive dielectric between two conductive states as means of storing logical data [3]. Device formation involves the dissolution of silver or copper in a chalcogenide (e.g., germanium selenide, germanium sulfide) or oxide (e.g., tungsten oxide) base glass to create a solid electrolyte. A silver-or copper-containing layer and an inert electrode formed in contact with the electrolyte film creates a device in which information is stored via electrical changes caused by the oxidation of silver or copper metal and reduction of silver or copper ions in the electrolyte [1].

2. PRINCIPLE OF OPERATION
Resistance-variable devices, in which a conductive path is formed or ruptured electrochemically, have been proposed by various groups for potential application to nonvolatile memories and switches. In 1976, Hirose *et al.* reported the first resistive switch, metal ions can migrate and an electronic conducting path is formed or rupture by applying a positive or negative voltage to the electrode. An electrode is an electronic conductor, while an ionic conductor is referred to as solid electrolyte. The device is composed of a Ag_2S (solid electrolyte) sandwiched by Ag and Pt or Au. Applying a positive voltage to the Ag electrode oxidizes the Ag metal at the interface between the Ag_2S and Ag electrode as shown in Fig. 1.

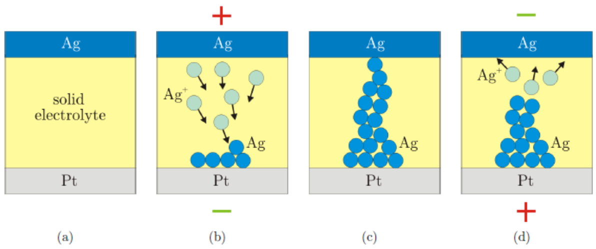

Fig 1: Graphic view of the switching process in an electrochemical memory cell with an oxidizable Ag electrode and an inert Pt electrode. (a) Off state; (b) switching on; (c) on state; (d) switching off.

When applied positive voltage on Ag electrode, Ag^+ ions are dissolved into Ag_2S according to the flowing equation:

$$Ag \rightarrow Ag^+ + e^-$$

On the Pt or Au electrode, Ag^+ ions are reduced and precipitated according to the flowing equation:

$$Ag^+ + e^- \rightarrow Ag$$

The precipitated Ag grows to form a conducting bridge between the Au and Ag electrodes, as shown in Fig.1. This puts the switch in the ON state. Subsequently, when a negative voltage is applied to the Ag electrode, the reverse reactions occur, and the bridge is dissolved into Ag_2S. Then, the switch turns off. The characteristic of the switching mechanisms is shown in Fig.2 [4].

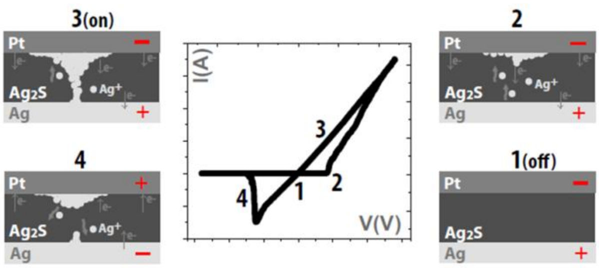

Fig 2: Current voltage characteristic of resistance switching caused by redox processes at the solid electrolyte-electrode interface [4]. The numbers from 1 to 4 indicate the order of the events.

The basic mathematical equations of the *i–v* characteristic for a current-controlled are:

$$v=R(w)i \quad (1)$$

$$\frac{dw}{dt} = i \quad (2)$$

Where w is the state variable of the device and R is the generalized resistance. It can be claimed that the state of the device is not only determined by the itself, but also the external bias conditions. The history of the bias conditions and previous device state will determine the following state. In general, the device is described by equations:

$$v=R(w,i)i \quad (3)$$

$$\frac{dw}{dt} = f(w,i) \quad (4)$$

Where w is a set of state variables and R and f are explicit functions of time. A resistive switching memory device can be seen as a serial connection of a high resistance part and a low resistance part as shown in Fig.3 [5].

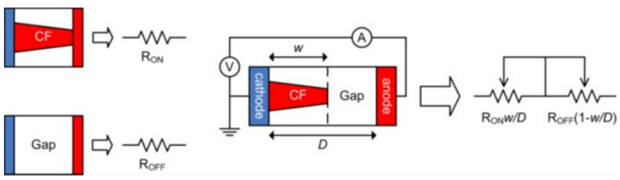

Fig 3: Simplified equivalent circuit of the coupled variable-resistor model [5].

When the external voltage bias varies the boundary of the two resistive parts moves. The physical mechanism of the moving boundary is the ion migration in high electric field in the electron insulating and ion conductive solid electrolyte. The mathematical models of the resistive switching phenomenon are [6]:

$$v(t) = \left(R_{ON}\frac{w(t)}{D} + R_{OFF}\left(1-\frac{w(t)}{D}\right)\right)i(t) \quad (5)$$

$$\frac{dw(t)}{dt} = \mu_V \frac{R_{ON}}{D} i(t) \quad (6)$$

$$w(t) = \mu_V \frac{R_{ON}}{D} q(t) \quad (7)$$

Where R_{ON} and R_{OFF} represents the low and high resistances of the resistive switching device, D will be the thickness of solid electrolyte, w is the thickness of doped or low resistive region of solid electrolyte, μ_V is the average ion mobility and q is the electronic charge.

3. DEVICE FABRICATION

The fabrication method to growth of Ag2S thin film is chemical bath deposition (CBD), which sulfurization the silver (Ag) by saturated solution of sulfur (S). When put silver layer in solution dissolved by sulfur, sulfurization starts with a direct reaction of Ag atoms under different time and temperature conditions forming an Ag2S layer. It can be noticed that sulfurization is defined as the conversion of elemental silver (Ag) films to silver sulfide (Ag2S) by reaction with molecular sulfur (S).

$$2Ag + S = Ag_2S \quad (8)$$

In order to conduct solution based sulfurization, A solution based reaction medium needed. Sulfur is soluble in aromatic organic solvents such as toluene, anisole and technical grade α-terpineol, but insoluble in aliphatic solvents such as hexanes and tetradecane [7]. Table (1) shows the Sulfur solubilities in various aromatic solvents. For my study, Toluene-sulfur solutions selected because of low solvent cost and available in my lab.

Table 1: Sulfur Solubilities in various aromatic solvents

Solvent Name	Toluene	Anisole	α-Terpineol
Sulfur Solubility	~15mg/mL	~15mg/mL	<15mg/mL

It can be found that sulfur solutions have been prepared by dissolving pure sulfur powder in toluene at various concentrations (0.26M, 0.82M, and 1.2M) and temperatures. The stirring speed is 150 RPM in a 100 mol beaker, with different temperature using magnetic hotplate stirrer. Sulfur's solubility limit in toluene is approximately 0.46M at 25C but it increases to 1.2M at 80C. This set the upper bound on concentration at various temperatures. When increase the toluene temperature, the concentration of sulfur increase and increase solubility of sulfur. A thermal evaporator deposition used under conditions of low pressure to pre deposit gold (Au) bottom layer as cathode thickness is about 1000 A°, then Ag layer thickness is about 400 A°. The sample putted in toluene beaker which has saturated sulfur for different time with different temperature and different concentration depends on temperature degree as shown in Figure (4). After sulfurized the Ag layer, anode layer (silver Ag layer) deposited by thermal evaporator deposition method of thickness about 1000 A°. A silver (Ag) probe can be used as top anode electrode instead of depositing to test the samples.

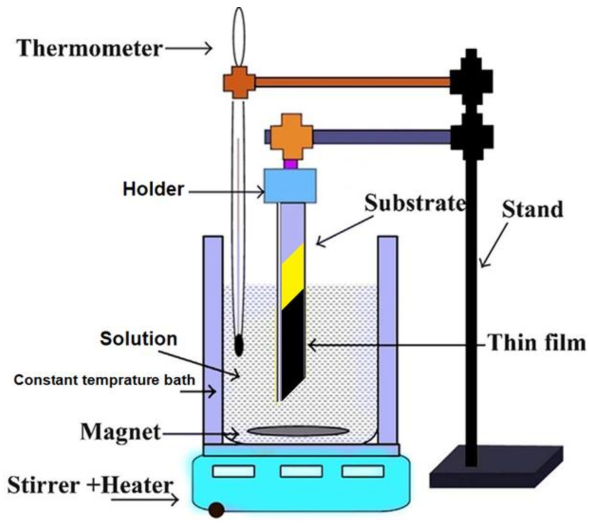

Fig 4: The Chemical bath deposition (CBD) for sulfurization.

A saturated solution gated by dissolving pure sulfur powder in toluene till stop dissolving the sulfur at specific temperature degree. Then the solution is filtered from the insoluble sulfur. A three samples sulfurized at deferent temperature start from room temperature with time 15 min, second one at 70C° with time 30 min and finally at 100C° with time 60 min. Upon removal from the bath, samples were rinsed with toluene to wash off the sulfur solution, then rinsed with acetone and isopropanol (IPA), and dried with compressed air.

4. RESULTS AND DISCUSSION

To measure the electrical properties of the fabricated samples (FS) Ag_2S devices, a simple electronic circuit used, for reading the voltage versus the current characteristics, presented in Fig.5.

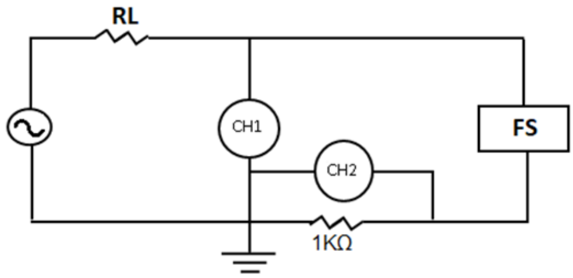

Fig 5: A Circuit used for testing the fabricated samples (FS)

The first method of the memory cell sample was fabricated under room temperature and within 15 min of reaction. We applied a triangulate signal voltage swept up to between -6V to +6V with frequency rate 0.1Hz on the cell to measure the I-V characteristics but not showed resistive switching. This is because the reaction time is short at low temperature of the solution, which is mean low solution concentration of sulfur show high leakage current.

Another sample memory cell was fabricated, with more sulfurized time, temperature and concentration of sulfur i.e. 30 min with 70C°. The results show an improvement in the I-V characteristic with switching resistance as shown in Fig.6.

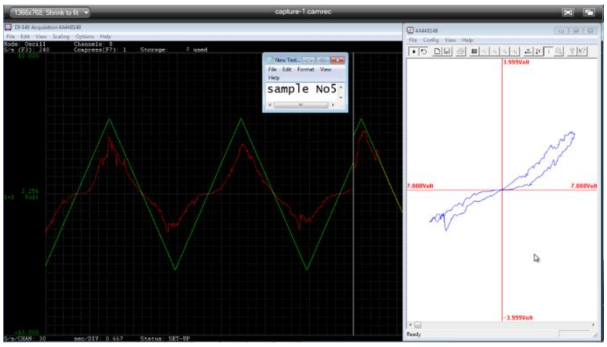

Fig 6: "The I-V Characteristic of the sample No.2 fabricated by CBD.

The second fabricated sample using higher sulfurized time and temperature indicates the effect of increasing sulfurization on the obtained Ag_2S layer. The result obtained by this sample is the decreasing of the leakage current or impurity of the Ag_2S solid layer, also show resistance switching at 0.8V. The resistance ratio can be calculated as:

$$R_{off} = \frac{0.8\ v}{0.04\ mA} = 20\ K\Omega$$

$$R_{on} = \frac{1.5\ v}{0.52 mA} = 2.88\ K\Omega$$

Where the ratio of R_{off}/R_{on} is:

$$\frac{R_{off}}{R_{on}} = \frac{20}{2.88} \cong 7$$

The third sample was fabricated by increasing the temperature to about 100C° of the solution, increase time of sulfurization and concentration in order to increase the sulfurization rate. The results show a good improvement in sulfurization Ag layer.

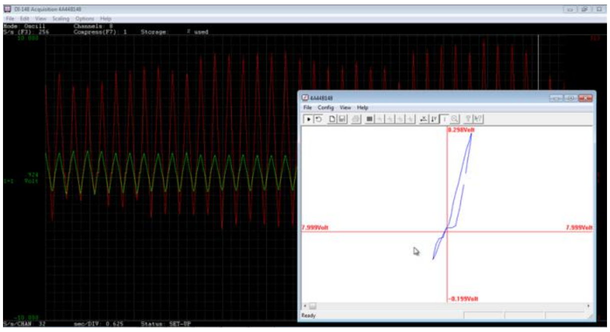

Fig 7: The I-V Characteristic of the sample No.3 fabricated by CBD.

We applied a triangulate signal voltage swept with amplitude voltage 2.5V and frequency rate 1Hz on the cell to measure the I-V characteristics. Noted that, the performance of the cell was improved to and switching voltage decreases to 0.5V. Figure (7) shows the I-V characteristics and it is clear that the ratio of high to low resistance increases and can be calculated as:

$$R_{off} = \frac{0.4\ v}{0.1\ \mu A} = 4\ M\Omega$$

$$R_{on} = \frac{0.7\ v}{160\ \mu A} = 4.375\ K\Omega$$

Where the ratio of R_{off}/R_{on} is:

$$\frac{R_{off}}{R_{on}} = \frac{4000}{4.375} = 915$$

To measure the switching time of the memory cell, (the transition from the OFF to the ON state switching time response), another test was accomplished by applying a square wave with a frequency of $1H_Z$ and amplitude 2V with DC shift 1V. We monitoring the current to the voltage characteristics transfer function using same setup circuit shown in Fig. (5).

Fig. (8) shows that the green line represents the memory cell voltage. The red line represents the current flow in the memory cell. Switching time measured by voltage drop across the cell to the level that satisfies the switch ON and switch OFF stat or by jump of the current signal to satisfies the switch ON and switch OFF stat. It is clear that time difference between the starting pulse and the satisfied level is about (15ms). Also, reset negative pulses are needed (30ms) to switch OFF the cell. These values of switching time depend on the applied voltage and duration during switch ON and switch OFF. When increase signal amplitude and duration, switching time decrease and vice versa.

Fig 8: I-V characteristic for ($Ag/Ag_2S/Au$) memory cell sample with switching time measurement with $L=200A^0$

5. CONCLUSION

The characteristic results obtained from experimental samples shows the conductive bridging memory cell (CBRM) is an attractive memory technology that offers simple integration and scalable operational condition. The fabricated Ag2S/Ag structure memory cell shows an ON resistance of about 4Ω and an OFF resistance of about 4MΩ which make this structure as a candidate future memory cell with high speed and low power consumption.

6. REFERENCES

[1] Michael N. Kozicki, Chakravarthy Gopalan," Non-Volatile Memory Based on Solid Electrolytes," Center for Solid State Electronics Research Arizona State University.0- 7803-8726 0/1/04/$20.00©2004 IEEE.

[2] Massood Tabib-Azar, and Yan Xie," Non-Volatile Solid-Electrolyte Memory Devices: Electronic versus Optical Latent Image Formation in Silver Halides," Case Western Reserve University Cleveland, Ohio 44106.ECS-Trans.3,28 2006.

[3] Chakravarthy Gopalan, Yi Ma, Tony Gallo," Demonstration of Conductive Bridging Random Access Memory (CBRAM) in Logic CMOS Process," 978-1-4244-6721- 1/10/$26.00 ©2010 IEEE.

[4] R. Waser, R. Dittmann, G. Staikov and K. Szot, Adv. Mater. 21 2632 (2009).

[5] D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, "The missing memristor found," Nature, vol. 453, no. 7191, pp. 80-83, May 2008.

[6] Tong Liu "Nonvolatile and Volatile Resistive Switching Characterization, Modeling, Memristive Subcircuits" Ph.D. thesis. Electrical Engineering department in Virginia Polytechnic Institute and State University. April 29, 2013.

[7] Shong Yin "Solution Processed Silver Sulfide Thin Films for Filament Memory Applications" Ph.D. thesis, Electrical Engineering and Computer Sciences University of California at Berkeley, December 17, 2010.

[8] Agnes GUBICZA, Resistive switching phenomena in Ag_2S based nanojunctions, Ph.D. thesis, Budapest University of Technology and Economics, Institute of Physics, Department of Physics (2016)