Fabrication and Study of Memory Cell Switching Properties Based on Cu_2S Compound

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Abstract

A variety of materials having large 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 tens of nm. This paper presents experimental results for solid state devices based on copper sulfide (Cu_2S) I-V characteristics.

Keywords: Cu_2S memory cell, non-volatile memory

تصنيع ودراسة خواص المفتاحية لخلية ذاكرة خزن مبنية على المركب Cu_2S

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الخلاصة

في هذا البحث تم اختبار مادة كبريتيد النحاس عن طريق تسليط جهد كهربائي عبر طرفي قطبين بينهما مادة كبريتيد النحاس, حيث يتم تغيير طور المادة من البلورية الى الحالة غير المتبلورة وبالتالي تغير مقاومة توصيل المادة. حيث يتم عملية الخزن عن طريق قياس مقاومة التوصيل للمادة, حيث يمكن الحصول من هذه المواد على خلايا خزن ذات فولتية قليلة وسرعة اداء عالية واستهلاك قدرة قليلة مع ثبات بالخواص مقارنة مع الانواع التقليدية لخلايا الخزن.

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1. Introduction

Physical size reduction of memory based on charge storage 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].

1.1 Principle of Operation

Resistance-variable devices, in which a conductive path is formed or annihilated 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 annihilated by applying a positive or negative voltage to the electrode. Cu is more compatible with current interconnect technology than Ag. The switch is composed of a $Cu_{2-\alpha}S$ sandwiched by Cu and Pt . Applying a positive voltage to the Cu electrode oxidizes the Cu metal at the interface between the $Cu_{2-\alpha}S$ and Cu electrode Fig. 1

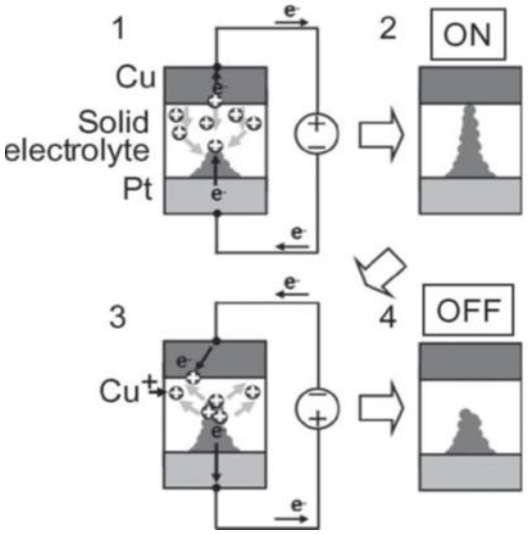

Fig. (1) Schematic view of the operation principle of the solid-electrolyte switch 1,2 ON state 3,4 OFF state.

$$Cu \rightarrow Cu^{+} + e^{-}$$

Cu^{+} ions are dissolved into $Cu_{2-\alpha}S$ on the Cu electrode. On the Pt electrode, Cu+ ions are reduced and precipitated

$$Cu^{+} + e^{-} \rightarrow Cu$$

The precipitated Cu grows to form a conducting bridge between the Pt and Cu electrodes, and the current flowing between them increases steeply at 0.14 V as shown in Fig.(1). This puts the switch in the ON state. Subsequently, when a negative voltage is applied to the Cu electrode, the reverse reactions occur, and the bridge is dissolved into $Cu_{2-\alpha}S$. Then, the switch turns off at −0.11 V [4]. The characteristic of the switching mechanisms are shown in fig. (2)

When a positive voltage is applied to the Cu electrode, a Cu bridge is formed and the switch is turned on. Cu+ ions are supplied via an electrochemical reaction at the solid-electrolyte/Cu interface. When a negative voltage is applied to the Pt electrode, the Cu bridge dissolves into the solid-electrolyte and the switch is turned off. (b) Linear and logarithmic current–voltage curves of $Cu_{2-\alpha}S$ switch.

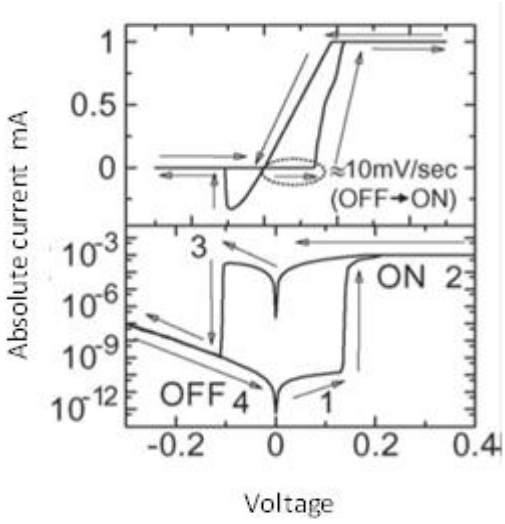

Fig.(2) I-V curve

Current J associated with charged ion i is given by

$$J_i = -\sigma_i \frac{\partial U}{\partial X} \quad (1)$$

Where σi is the conductivity corresponding to different charged particle, The equation (1) essentially is Ohm's Law and the total conductivity σt then

$$\sigma_t = \sum_i \sigma_i = \sigma_{Cu^+} + \sigma_{Cu^{2+}} + \sigma_{S^{2-}} + \sigma_e \quad (2)$$

The ion conductivity (σ_{ion}) in Cu_xS system thus can be described as

$$\sigma_{ion} = C_{ion}\, \mu_{ion}\, Z_{ion}^2\, q \quad (3)$$

Where C_{ion} and μ_{ion} are ion concentration and mobility respectively,Zion equals to 1~2,corresponding to CuS, Cu_xS and Cu_2S (x ranges between 1 and 2)[6].

The flux of Cu in Cu_2S is described as [4]

$$J_{Cu^+} = -\frac{D_{Cu^+}}{RT} \nabla\left(RT\ ln\, a_{Cu^+}^{Cu_{2S}} + F_{ZCu}\, \emptyset^{Cu_{2S}} \right) \quad (4)$$

where D: is the diffusive coefficient, a: is the activity, factor φ: is the electric potential, R: is the gas constant, T: is the temperature, F: is Faraday's constant, and z: is the valence. Assuming a redox reaction between Cu and Cu at the Cu/Cu_2S interface, the flux across an interface with width Δy is defined as

$$J_{interface} = \frac{-M\left\{ F_{ZCu}\, \emptyset^{Cu} - \left(RT\ ln\, a_{Cu^+}^{Cu_{2S}} + F_{ZCu}\, \emptyset^{Cu_{2S}} \right) - F_{ZCu}\, E^{excess} \right\}}{\Delta y} \quad (5)$$

where M is the average of the motilities of Cu in Cu_2S. E excess represents the sum of the standard electrode potential and the over potential. In addition, the distribution of the electrical potential is obtained by solving the equation of charge conservation for the entire region (i.e., Cu, Cu_2S, Pt, and the void) simultaneously. The electric currents, are described as[5]

$$\nabla . i_j = 0 \quad (6)$$

$$i_h = -\frac{\sigma_h}{F z_h} \nabla (RT\ \ln p + F_{Z_h} \emptyset) \quad (7)$$

$$i_{e^-} = -\sigma_{e^-} \nabla \emptyset \quad (8)$$

Where (i_j) in Cu_2S are regarded as hole conduction and in other regions are regarded as electron conduction.

Where σ: is the electric conductivity, and p: is the hole concentration, defined by the defect chemical equation as

$$p = (K\ a_{Cu})^{-1/2}$$

Where K is the equilibrium constant [5] These features are advantageous in programmable LSI circuits, such as a field programmable gate array (FPGA). An FPGA is composed of reconfigurable logic cells and interconnections that are programmed by a large number of switches [5].

A numerical of solution equation (10) [6]of the partial differential equation can be obtained using Matlab to get a copper concentration with varied time and distance as shown in fig.3

$$\frac{\partial C_{ion}}{\partial t} = D_{ion}\frac{Z_{ion}qv}{R\,T}\left(\frac{\partial C_{ion}}{\partial x_\circ}\frac{1}{L-x_\circ}\frac{C_{ion}}{(L-x_\circ)^2}\right) \quad (10)$$

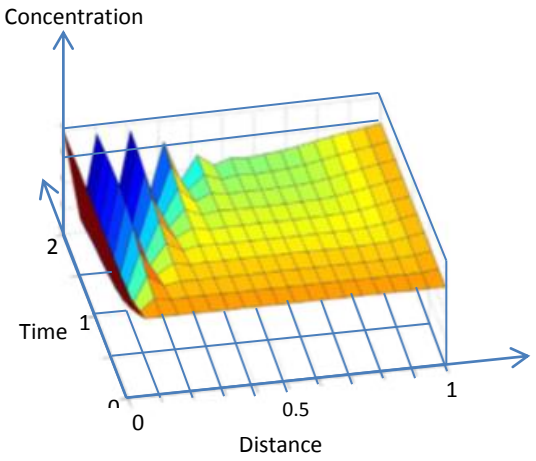

Fig. (3) Numerical simulation of concentration versus distance and time with low voltage and high voltage

2. Device Fabrication

Two structure cells were fabricated on glass substrates as shown in fig.(4). The first structure cell was composed of the copper layer with thickness of 2000A° and Cu_2S layer with different thickness (700- 1000A°).The inert electrode is fabricated from aluminum metal and gold material for another structure instead of platinum Pt . The second structure is fabricated in a different form as shown in fig.(4b),the Cu layer thickness is about 2000A° while the Cu_2S layer thickness is about 400 A° . The top contact electrode was fabricated from gold material with thickness of about 1000 A°.

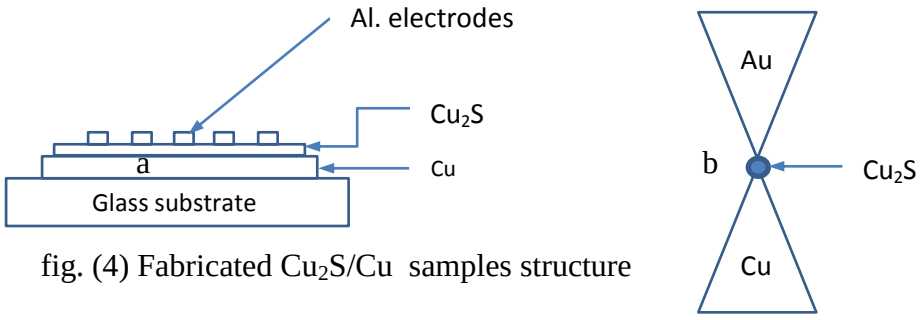

fig. (4) Fabricated Cu_2S/Cu samples structure

The Cu_2S layer of thickness 500A° is then deposited by evaporating copper and sulphur from two separate tungsten and molybdenum boats. Fig.5 shows the arrangement for evaporation of copper and sulphur, copper is placed on the tungsten boat which is resistively heated using a low tension power supply. Sulphur is placed on molybdenum boat with a cover and a small opening on top. The sulphur source is placed at a distance of about 3 cm above the copper source. When the copper source is heated it also indirectly heats the boat containing sulphur and the simultaneous evaporation

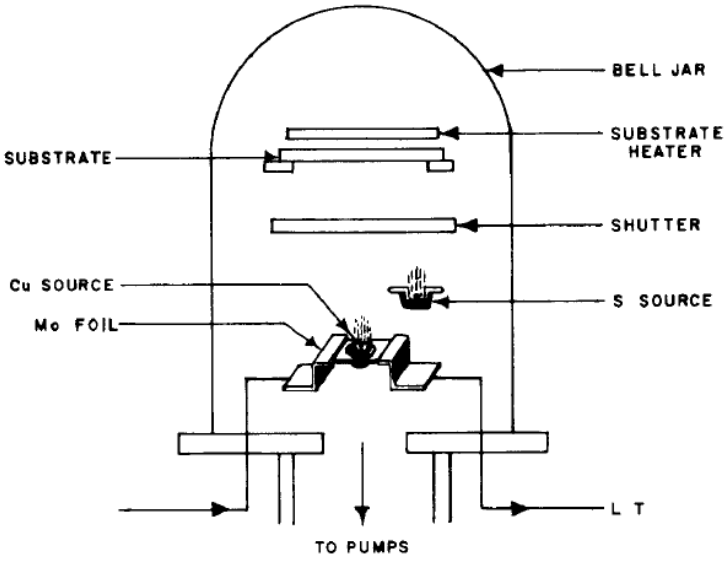

Fig (5) Bell jar balzer equipment

of copper and sulphur starts. The shutter is then removed to ensure deposition of Cu_2S on the substrate. The substrates are maintained at room temperatures for 15 min. the sample tested using pico ampere meter Khithley 6487 to measure the I-V characteristic.

3. Results and discussion

The I-V characteristic of the Cu_2S/Cu structure (sample1) is shown in fig.(6). A negative voltage is applied to the Cu electrode with respect to Al electrode, it is clear that the sample has a small memory effect noticed in forward direction characteristics. The behavior characteristics are looking like linear resistor when the thickness is about 1000A°. Fig.(7) shows the I-V characteristics of the Cu_2S/Cu structure with 700A° thickness. The memory effect is increased in forward and reverse direction because the Cu filament bridge construct quickly and the cell transfer from OFF state to ON in wide current range. Both samples also tested in AC triangular voltage (1kHz) source to insure positive and negative voltage sweep, the two characteristic is shown in fig. (8&9) .

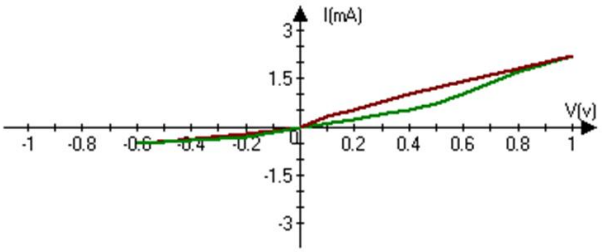

Fig.(6) I-V characteristic of Cu_2S/Cu structure structure with Cu_2S thickness of 1000A°

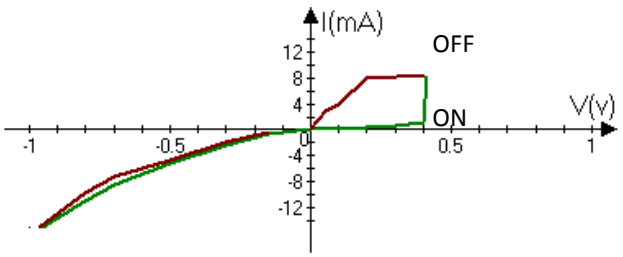

Fig.(7) I-V characteristic of Cu_2S/Cu with Cu_2S thickness of 700°

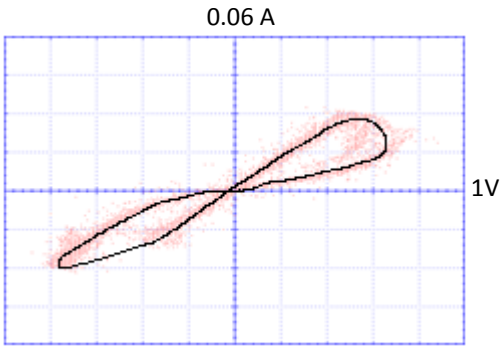

Fig.(8) I-V characteristic of Cu_2S/Cu structure with triangular voltage source (1kHz) Cu_2S thickness =1000A°

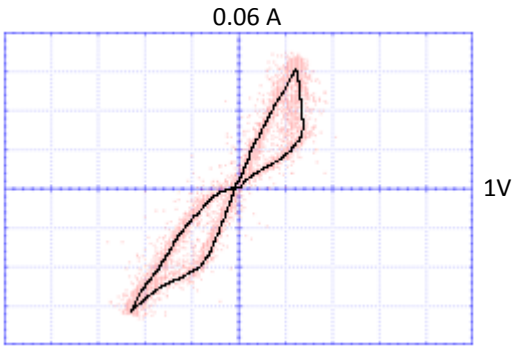

Fig.(9) I-V characteristic of Cu_2S/Cu structure with triangular voltage source (1kHz) Cu_2S thickness =700A°

Fig. (10) and fig.(11) shows the DC and AC characteristics respectively of the Cu_2S/Cu structure with a thickness of 400A°. The memory effect is increased clearly and the ON resistance is measured and found to be (10Ω),while the OFF resistance is more than (100kΩ).

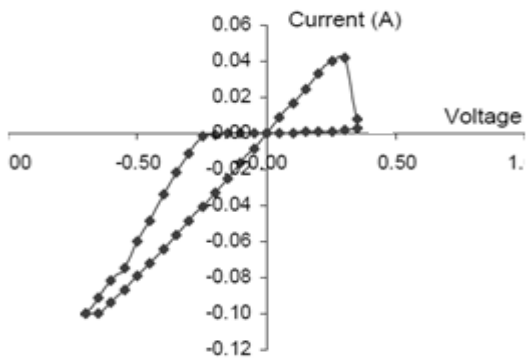

Fig.(10) Dc characteristic of Cu_2S/Cu with with Thickness=400A°

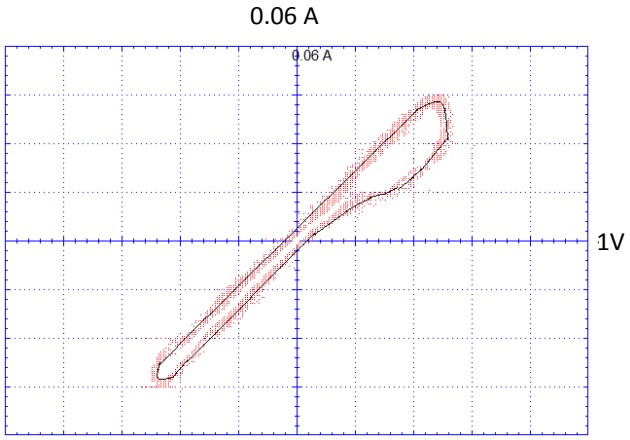

Fig.(11) Dc characteristic of Cu_2S/Cu with Thickness=400A°

The last results prove the validity of using the Cu_2S/Cu structure as high speed and low power memory cell, the low voltage swing of the cell between the ON and OFF state make these cell structures an attractive one because the transition between one and zero will take very short time compared to all other cell (very high speed logic).

Conclusions

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 Cu_2S/Cu structure memory cell shows an ON resistance of about 10Ω and an OFF resistance of about 100kΩ which make this structure as a candidate future memory cell with high speed and low power consumption.

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