Printable ReRAM devices based on the non-stoichiometric junction CuS/$Cu_{2-x}S$

M. Congiu✉, L.G.S. Albano, O. Nunes-Neto and C.F.O. Graeff

Hereby a novel thin film-based configuration of redox resistive switching memory (ReRAM) based on cheap and abundant copper sulphide (CuS) is reported. The devices working mechanism is based on the junction of two layers of CuS stacked nanocrystal with different stoichiometry (CuS and $Cu_{2-x}S$). CuS thin films were deposited using a fast, easy and low-temperature drop-casting technique. The devices shown memresistive characteristics, with well-defined ON and OFF resistance states, inducible by voltage pulses. A polynomial model has been proposed to characterise the devices considering both space-charge-limited current and ionic diffusion.

Introduction: The theory of memristors (MEMs) was proposed by Chua *et al.* in 1971 [1] 'the missing element' in the circuit's theory, capable to fill the missing relationship between the charge $Q(t)$ and the current flux $J(t)$. MEMs remained just a theoretical object until its realization in 2008 by the HP labs [2]. Resistive switching memories (RRAMs) belong to MEM's family and are an interesting and multidisciplinary topic of modern scientific and technologic research. In fact, RRAMs could be applied in some field of technology such as memory storage [3], computing and logic operations [4] and neuromorphic computing applications [5]. An RRAM is a resistive element whose resistance can be varied by applying a voltage pulse [2]. In most real cases, the devices present two states: a higher resistance state (HRS) and a lower resistance state (LRS). The respective resistances of the above-mentioned states are defined as R_{ON} and R_{OFF}. Thus, the device can be used as a Boolean logic switch returning (0) when the resistance is R_{OFF} value and (1) when R_{ON} [4]. In RRAM, the information is stored over time (non-volatile memory). An interesting kind of RRAM is the redox resistive switching memory (ReRAM) [6]. In this specific device, the different resistance states are induced by a redox reaction within the composing materials [7]. Copper sulphides (Cu_xS) belong to a group of cheap and interesting materials in the field of RRAM and ReRAM. In fact, recent studies have demonstrated the applicability of Cu_xS in memory switching devices [8]. Within this work we propose a novel ReRAM configuration based on the junction of two layers of copper sulphide (CuS) with different stoichiometry: CuS and $Cu_{2-x}S$. The method used for the film deposition is based on a cheap suspension of hexagonal CuS nanocrystals (NCs) directly drop-casted on the substrate.

Materials and methods: $CuSO_4 \bullet 5H_2O$ (≥98%); thioacetamide (TAA); *F*-doped tin oxide (FTO glass slides ~7Ω/□); $NaCH_3COO \bullet 3H_2O$ (≥99%) and CH_3COOH 99–100% from Sigma-Aldrich. Sodium thiosulphate ($NaS_2O_3 \bullet 5H_2O$ ACS; $CuCl_2 \bullet 2H_2O$ and absolute ethanol from Synth, Brazil. Acetylacetone and dichloromethane from Merck Millipore. Current against voltage (*IV*) curves were registered using Autolab PGSTAT 302. Stacked hexagonal CuS NCs have been prepared through the precipitation reaction between TAA (water) and Cu(II)acetylacetonate (dichloromethane), following the method proposed by Basu *et al* [9]. The as-prepared green CuS NCs have been used to prepare a 5 mg/ml suspension in ethanol. The suspension has been sonicated during 30 min in order to promote the disaggregation of the crystal and avoid the fast formation of precipitates. The NCs suspension was dropped on the substrate (100 µl cm^{-2}), then it was placed into a vacuum chamber to promote the fast evaporation of ethanol. The as-obtained green layer of CuS NCs was annealed at 250°C during 30 min in order to obtain the non-stoichiometric phase $Cu_{2-x}S$ (yellowish) [10]. After cooling, another layer of CuS NCs was deposited on the as-prepared $Cu_{2-x}S$ following the same procedure described above but using a lower annealing temperature (100°C). The lower annealing temperature does not affect the stoichiometry of CuS NCs. Finally, a 100-nm-thick aluminium (Al) layer was deposited by evaporation at a base pressure of 5×10^{-6} torr on top of CuS NCs layer. The geometry of Al electrode was controlled using a shadow mask; the active area of the MEM is determined by the overlap of two electrodes, 2 mm^2.

Results and discussion: The memresistive behaviour of the devices has been investigated through current against voltage measurements, as shown in Fig. 1. In this configuration, when a positive voltage bias is applied, the current starts to grow with an ohmic trend up to 6.8 mA at 1.2 V. After this threshold voltage, the current drops abruptly and remains below 0.6 mA up to 4.0 V and also in the rest of the CV cycle from 4.0 to −1.5 V. Current starts to grow again when voltages more negative than −1.5 V were applied during the scan. When the CV scan comes back from −5.0 to 0 V, the curve shows a higher slope. According to the CV results, the device shows two different resistance states in the range from 0 to −1.2 V.

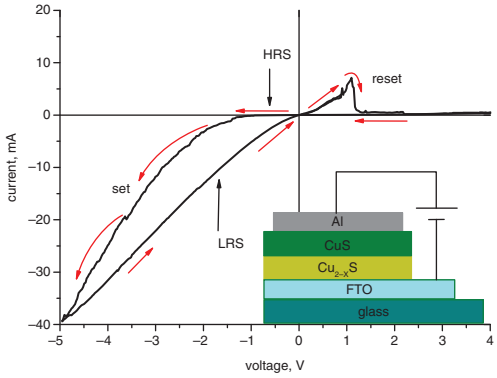

Fig. 1 *Cyclic voltammetry of proposed memristor device. Scan was performed at 100 mVs^{-1} from 4.0 to −5.0 V. Red arrows represent scan cycle direction. CV scan starts from 0 V and goes to positive voltages. In this region, it is possible to see abrupt drop of current and device is set in HRS. At negative voltages, device is set to LRS*

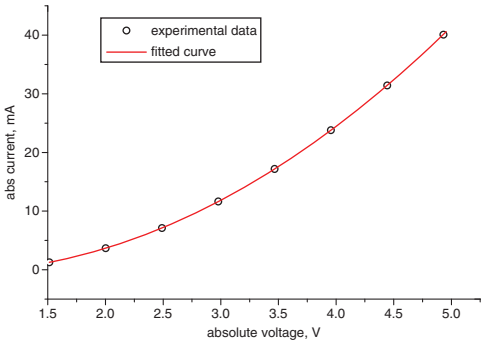

Fig. 2 *Current against voltage curve in range from −1.5 to −5.0 V. Note that in all plots just absolute value (abs) have been reported. Dots represent experimental data, whereas continuous line represents polynomial model used to fit curve*

This behaviour could be explained considering the p-type nature of Cu_xS ($1 < x < 2$). In fact, in most Cu_xS the majority charge carriers are holes, generated by Cu vacancies [11]. When a positive sweep is applied to the cell, the electrons flow from the anode ($Cu_{2-x}S$) to the cathode (CuS). Looking at Fig. 1, the first part of the curve, the abrupt drop of the current at 1.2 V could be addressed to the recombination of holes with electrons at the interface CuS/$Cu_{2-x}S$. The depletion of the majority charge carrier from the interface between CuS and $Cu_{2-x}S$ makes the CuS layer more resistive and this explains the transition from LRS to HRS seen in the first part of the CV curve. The LRS is re-established after a negative voltage sweep. Looking at the negative part of the *IV* curve (Fig. 1), during the transition from HRS to LRS, the current shows a quadratic dependence on applied voltage ($I \alpha V^2$) from −1.5 to −5.0 V. This suggests that the transition from HRS to LRS can be described by space-charge-limited current, also observed in the p-type Cu_xO [12]. This effect is predominant when the injected charge carriers (holes) density is higher than the density of the thermally generated ones. In this condition, the current flux J (mA cm^{-2}) is driven by the shallow trap square law described in (1)

$$J = \frac{9\varepsilon_r \varepsilon_0 \mu V^2}{8L^3}\left(\frac{N_c}{N_t}\right)e^{(-E/kT)} \quad (1)$$

where ε_r and ε_0 are the static dielectric and the vacuum permittivity constants, respectively; μ is the hole mobility; L is the film's thickness; N_c is the density of the states in the conduction band; N_t is the density of trap states with the trap energy E and V represents the applied voltage. When

the negative voltage sweep is applied to the device, holes coming from the $Cu_{2-x}S$ (cathode) are injected into CuS (anode) at the interface between the two layers. The non-stoichiometric Cu(I)/Cu(II) phase of $Cu_{2-x}S$ layer allows to generate the excess of holes into the CuS layer. The *IV* response corresponding to the HRS→LRS transition is presented in Fig. 2*a*.

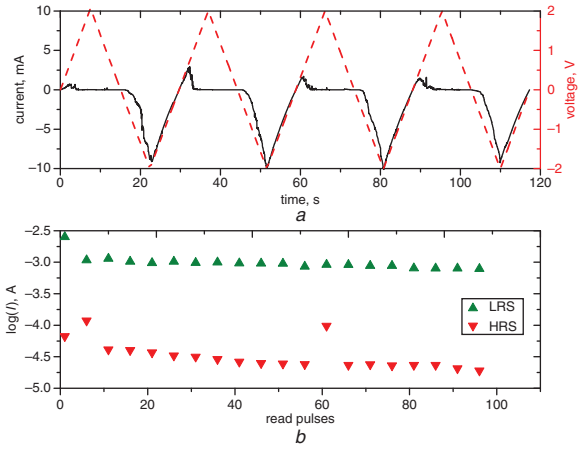

Fig. 3 *Electrical tests of the memory storing capability of the device proposed within this work. LRS and HRS states have been inducted applying both continuous and pulsed waveforms*

a 50 mVs^{-1} (33.6 mHz) triangular voltage wave applied to device and current was registered between −2 and 2.0 V

b Logarithmic plot of current values of LRS and HRS during 100 read/write cycles

The fitting of experimental curve was performed using a polynomial equation as reported in (2)

$$I = aV^2 + bV + c \tag{2}$$

A linear additive voltage-dependency term (bV) and a constant c have been considered to improve the fitting of the experimental curve. The presence of a linear term bV could be explained by considering the flux (J) generated by Cu^+ cations, which have high mobility through the sulphide film [13]. The flux J, generated by the diffusion of Cu^+ ions within the film can be written as (3)

$$J = -\frac{q}{kT} V D_0 C_0 e^{-((E_d - E_s)/kT)} \tag{3}$$

where q is the charge of the ion; V is the applied voltage; D_0 and C_0 represent the diffusion and the solubility constants in the considered medium; E_d and E_s are, respectively, the diffusion and the solubility energies; k is the Boltzmann's constant and T is the temperature. During the transition HRS→LRS, Cu^+ cations can diffuse from the bulk of the $Cu_{2-x}S$ film to the FTO contact generating thus an ionic current that adds to the electronic current. The constants a and b, obtained from the fitting, considering an area of 0.14 cm^2, are: a = 15.7 mA cm^{-2} V^{-2}(1), b = −20.2 mA cm^{-2} V^{-1} (2) and c = 3.57 mA cm^{-2}. At the end of the negative sweep, when the voltage varies from −5 to 0 V, the current shows a quasi-linear behaviour ($I \propto V$) in the range from −5.0 to −1.0 V. In this ohmic range, the resistance is approximately 113 Ω. This behaviour is reproducible even after repeated CV cycles (Fig. 3*a*).

As shown in Fig. 3*a*, it is easy to distinguish both the LRS and HRS states during the voltage transients. To investigate the storage capacity of the voltage-induced LRS or HRS, the device has been submitted to repeated reading measurements. The LRS was induced (set) by applying two successive square voltage pulses (−5.0 V, 1 s). Then, repeated reads of the current at −1.0 V have been performed during 10 ms. Between the pulses, a delay of 10 s at 0 V was used. After the LSR measurements, two pulses of +5.0 V (1 s) have been applied in order to set the device in an HRS state (reset). As shown in Fig 3*b*, the device stored the induced state over the considered time applying up to 100 square read pulses (−1.0 V, 10 ms). As can be seen, there is a significant difference between the currents in the HRS state compared with the LRS state, which shows the good potential of our device as an ReRAM.

Conclusions: These results constitute the starting point of a future and more in-depth investigation in order to improve the device's performance. In this direction, different deposition methods and different thicknesses of Cu_xS films will be studied in order to improve the LRS→HRS transition reducing the switching time.

Submitted: *9 August 2016* E-first: *30 September 2016*
doi: 10.1049/el.2016.2901
One or more of the Figures in this Letter are available in colour online.

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