Growth of copper sulfite thin films as active layer of memristor device

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Introduction

In 1971 Leon O. Chua proposed the existence of a fourth two-terminal passive fundamental electronic element [1], the memristor - a non linear resistor for which the resistance state depends on the history of the applied voltage. The experimental discovery of the memristor by Strukov et al. [2], almost 40 years later, marked the beginning of a new and multidisciplinary research field with a scientific community that consistently increase each year. Besides its research on the fundamentals of the inner principles involved in the memristor physics, this novel device opens new perspectives in applications, such as neuromorphic hardware that have the ability to simulate a biological neural network [3]. The structures that are used in most memristive devices are MIM (metal-insulating-metal) structures, characterized by an active insulating layer, separating two metallic electrodes. Due to the simplicity of this structure, memristive devices with different active layers were developed, among them we can mention: metal oxides [2], chalcogenide systems [4], solid electrolytes [5] and even organic compounds[6]. In this work we present a study of the fabrication process and the electrical transport properties of a copper sulfide based memristor. We used different approaches to fabricate the copper sulfide active layer: solid-state reaction using sulfur powder on a copper surface and chemical bath deposition (CBD). We will approach as responsible for the transition between states of resistance the electrochemical metallization model(ECM)[7].

Objectives

- This work aims to manufacture a low cost memristor with an active layer of copper sulfide, based on a new planar device architecture;
- Perform an electrical characterization of the memristor device in order to understand the dominant mechanism of electronic transport;
- Understand the statistical nature of resistance state switching;
- Apply in neuromorphic circuit in the future;

Prototype memristor

Preliminary studies were carried out on a memristor prototype from a polished copper substrate. The growth of the copper sulfide film was accomplished by solid contact between the sulfur powder and the polished substrate. The contact remained at room temperature for 22 days. After that time, a layer of copper sulfide was created over the substrate. Finally, an aluminum piece was placed on the film, making contact by pressure.(Figure(1)).

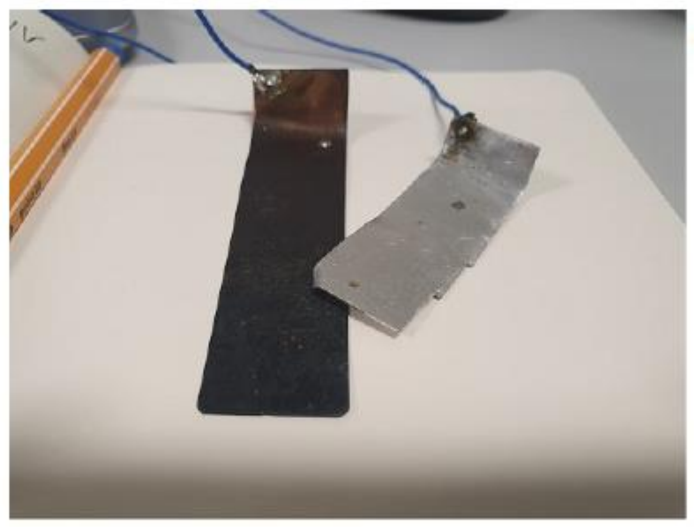

Figure 1. Image of the memristor prototype. We can visualize a copper substrate covered with a copper sulfide film using the powder chemical reaction method.

The memristors have a characteristic I-V behavior of a loop with current hysteresis depending on the frequency of the potential sent to their terminals (indicated by ref. [1]). This behavior is found in the electrical characterization measures of the prototype memristors that we manufacture.(Figure 2a)

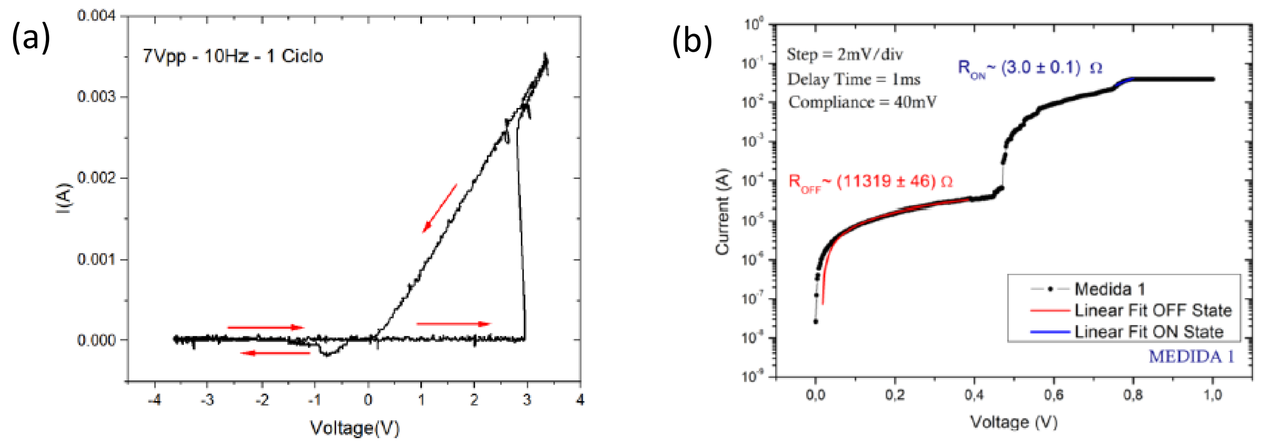

Figure 2.(a) Characteristic IV in memristors, observing a transition between resistance states IV (b)Current-voltage characterization measurement from a scan signal between -1V to 1V with a step of 2mv / division with a current compliance of 40mV with variations only in the waiting time for each 2mV rise of 1ms.

The ECM model consists of a migration of a metallic cation in an ionic conductor towards the cathode made of an inert material where it will be reduced. The atoms of the reduced metal form a metallic filament that grows towards the active anode and when the filament comes in contact with the anode, the resistance changes abruptly to a low resistance state (Figure 2a and b). The phenomenon of rupture and filament formation allows the appearance of a distribution the time in which the state transitions from the least conductive to the most conductive regime. This happens because the process of growth of the filament presents probabilistic characteristics. Our measures indicate the appearance of a lognormal distribution (Figure 3a and b). This result shows a dependence on the history of the filamentary bridge.

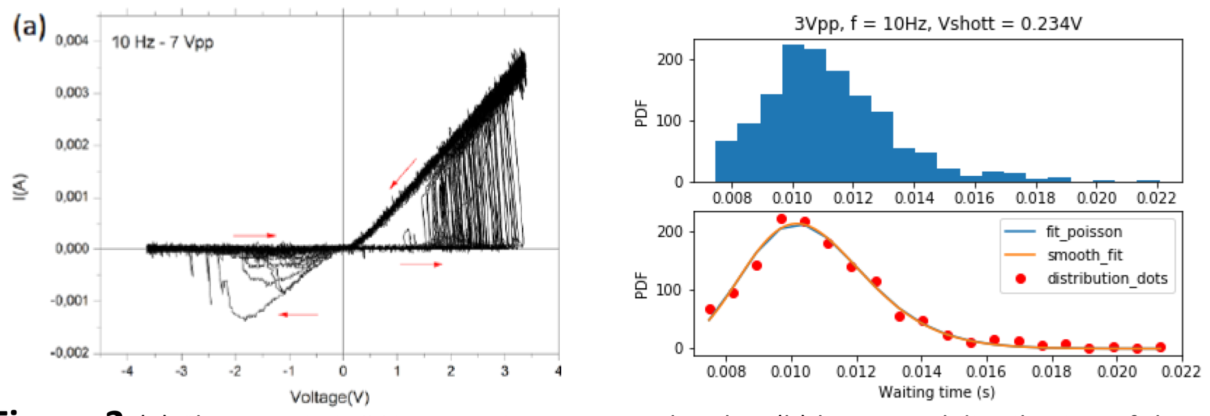

Figure 3.(a) Characteristic IV in memristors, several cycles. (b) lognormal distribution of the waiting time for the transition between the resistance states

Device architecture

The photolithography procedure for the manufacture of the memristor is divided into two stages: the deposition of copper according to the pattern shown in Figure 4, and the deposition of silicon demarcating the contour of the gap. As shown in Figure 1, we decided for a simple architecture, with three gaps with different sizes (5, 10, 15 μm), in order to investigate the influence of the spacing of the electrodes in the formation of the metal filaments. In addition, we performed a second photolithography as shown in Figure 1, after copper deposition in order to deposit a film layer on the silicon to protect the copper film from oxidation, due to contact with air.

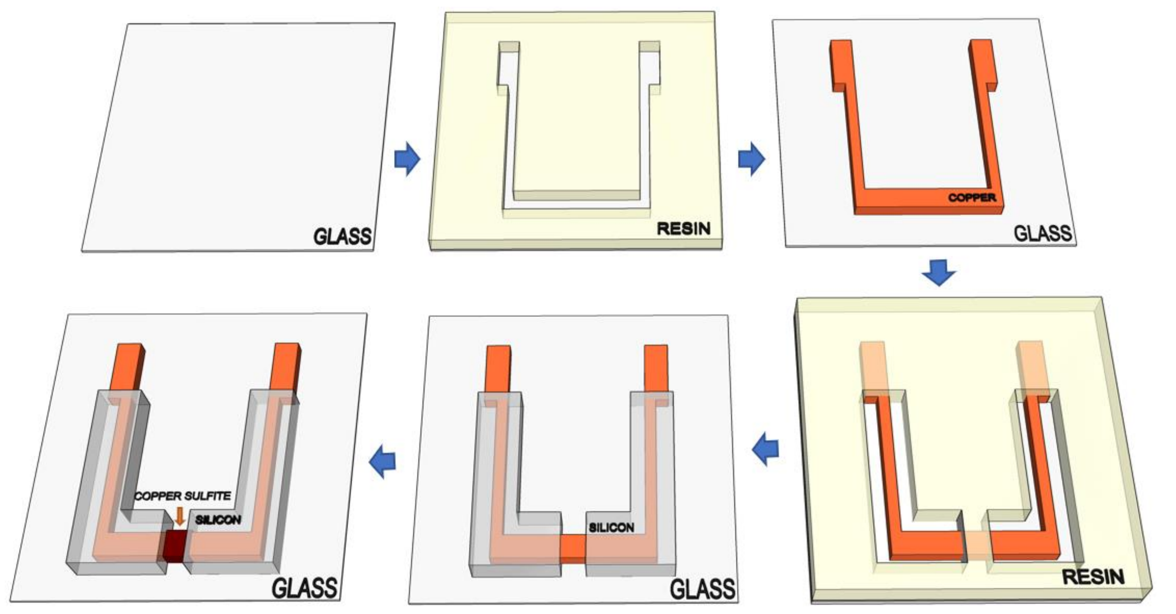

Figure 4. Image indicating the step by step of the microfabrication of the memristor device. Showing from the substrate through two lithography processes. And in the last figure it represents the device ready with the copper sulfide film present in the gap.

Growth of copper sulfite thin films

In our work, we used the script proposed by Vas-Umnuay and Chang [8] following the levels of molar concentration and the proportion of reagents for the formation of the copper sulfide film by the CBD method. We measure, using the two-wires technique, the electrical resistance as a function of the time of the microfabrics devices. At each 30-second time interval, we apply a small voltage to the terminals to measure the electric current, thus allowing the device to find the electrical resistance value. In the case of sulfur powder, as time progresses, the width of the copper channel decreases, due to the reaction of copper with sulfur. Therefore, the resistance shows the expected increase until close to 2000 seconds. With the gradual decrease of the channel, a moment will arrive in which the ohmic channel will disappear, changing the regime of electronic ohmic transport to hopping transport. As a result, there is a rapid increase in resistance compared to the ohmic regime. In this scenario, we propose that the increase in noise is associated with changes to electron hopping transport. For the other methods, we noticed a rapid increase in resistance during the first minutes; and the resistance remained in a constant order of magnitude for the next 26 minutes, but the 5 μm device revealed a shot in its resistance, possibly characterizing a break in the continuous copper path.

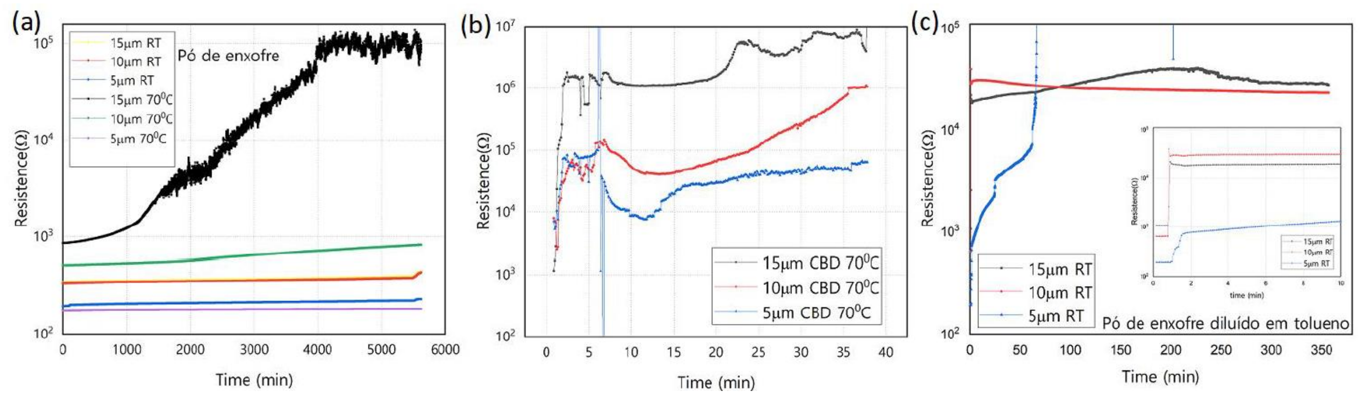

Figure 5. The graph indicates the evolution of the resistance of the devices during the chemical reaction by three different routes: (a) Sulfur powder, (b) deposition by chemical bath, (c) Sulfur powder diluted in toluene solution. The detail in (c) indicates that the toluene solution containing powder, in the first minutes, reacts quickly with the copper exposed on the substrate.

The appearance of a current hysteresis in microfabricated devices, as shown in Figure 6, makes the protocol adopted for the manufacture of memristors, both in terms of the design of the device architecture and the growth process of the copper sulfide film by CBD technique, promising for the next stages of the project.

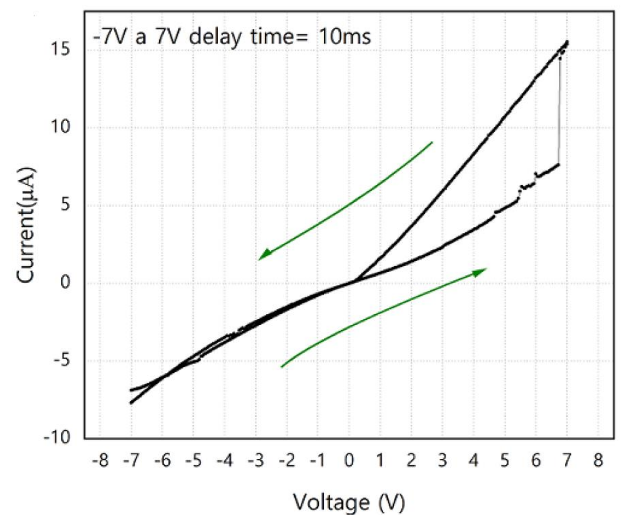

Figure 6. IV characteristics found in microfabricated memristors

Conclusions

The project, until now, managed from a new architecture to observe the main characteristics found in memristive systems. Therefore, the adopted protocol is successful. With that in mind, the next steps that we will address will be the more detailed investigation of the film produced in the gap region and adapting the device to neuromorphic circuits.

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