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Leiden
The Netherlands

Resistive switching in mixed conductors : Ag₂S as a model system

Morales Masis, M.

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Conductance switching in Ag_2S devices fabricated by sulphurization

The electrical characterization and switching properties of the α - Ag_2S thin films fabricated by sulfurization are presented in this chapter. The α - Ag_2S thin films show semiconductor behavior at low bias voltages, whereas they exhibit reproducible bipolar resistance switching at higher bias voltages. The transition between both types of behavior is observed by hysteresis in the IV curves, indicating decomposition of the Ag_2S and formation of a conductive path between the electrodes.

This chapter is partly based on M. Morales-Masis, S. J. van der Molen, W. T. Fu, M. B. Hesselberth and J.M. van Ruitenbeek, *Nanotechnology* **20** 095710 (2009)

3.1 Introduction

Silver Sulfide is a mixed conductor material, with the total conductivity (σ_t) determined by that of the Ag⁺-ions (σ_{Ag^+}) and electrons (σ_e), i.e. $\sigma_t = \sigma_e + \sigma_{Ag^+}$. In the low temperature phase, α -Ag₂S, the total conductivity increases with temperature representing semiconductor behavior.

Silver sulfide also presents conductance switching characteristics when a thin film of this material is placed between metal electrodes, and a sufficiently large voltage is applied. Previous studies [14] indicated that the conductance switching is of filamentary nature, meaning that switching occurs due to the reversible formation of a conductive path across the Ag₂S layer. The conductive path connects the electrodes causing the switching in conductance, and the persistence of the conductive path after the removal of the bias can be exploited for memory applications. As mentioned in Chapter 1, the requirements for this type of memories are the mobile metal ions (the Ag⁺-ions in the case of Ag₂S) and an asymmetry of the electrodes, defined either by the type of metal or by the geometry of the electrodes [5].

This chapter presents our study of the electrical properties of Ag₂S devices prepared by the sulfurization method (described in Chapter 2 Section 2.2). The chapter starts with the description of the measurement hardware and software. Next, conductivity measurements as a function of temperature are presented, serving for the electrical characterization of the sulfurized Ag₂S films. The last part of the chapter is dedicated to the conductance switching properties measured on devices of the form Pt/Ag₂S/Pt(micro-contact). In these devices, the asymmetry of the electrodes is imposed by the geometry, a large Pt bottom contact and a small Pt micro contact on top, and this asymmetry defines the voltage polarity at which the device switches ‘on’ or ‘off’. Bipolar switching (setting of the ‘on’ state at one voltage polarity and setting of the ‘off’ state at the reverse polarity) is studied for a range of bias voltages.

3.2 Measurement setup

To measure the electrical properties of the Ag₂S devices we used a simple electronic circuit, presented in Fig.3.1. It consists of a dc voltage source, for which we use an analog output of a National Instruments Data Acquisition Card (NI

USB-6251, M Series DAQ). The current through the sample due to the dc voltage applied is converted into a voltage using a FEMTO current amplifier (DLPCA-200 variable gain transimpedance [V/A] amplifier), and the output of the current amplifier is read by an analog input channel of the NI USB-6251 DAQ.

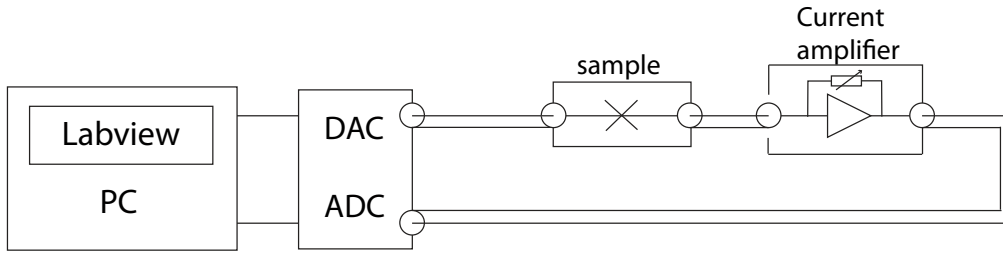


Figure 3.1: Schematic diagram of the measurement circuit.

The NI DAQ is programmed with the LABVIEW development package of National Instruments. The LABVIEW programs allow the simultaneous control of the bias voltage and the monitoring of the current input. For each experiment, a specialized LABVIEW program was developed according to the requirements for each of the measurements (e.g. waveform of the output voltage, frequency, sampling rate).

3.3 Electrical conductivity

Conductivity measurements as a function of temperature were performed for electrical characterization of the sulfurized Ag_2S films. For these experiments the samples were prepared with a specific electrode configuration, using two parallel electrodes (Pt and Ag stripes, 0.5mm width and 0.5mm separation) crossing the Ag_2S film (150nm thickness), as shown in the inset on Fig.3.2. The electrodes and Ag_2S were deposited on a mica substrate. Measurements were performed by applying an alternating voltage (± 50 mV square wave, 1 Hz) to the parallel electrodes, and by increasing the temperature in steps of 5 K starting at room temperature. In Fig.3.2 we present an Arrhenius plot for one of our samples. In the plot two slopes are observed: one in the temperature range from 299 K to 417 K and a second one for $T > 417$ K, where a steep rise in conductivity is observed. From the first slope (in the temperature range $299 \text{ K} < T < 417 \text{ K}$), the calculated activation energy for electrical conductance is 0.64 ± 0.03 eV, which

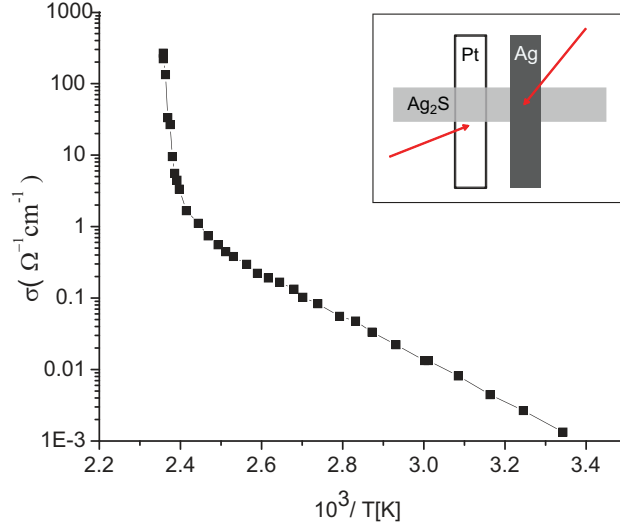


Figure 3.2: Arrhenius plot of the electrical conductivity of a Ag_2S film. The inset shows the electrode configuration used for the two-probe measurements. The arrows indicate the position of the contacts to the Pt and Ag electrodes.

is in close agreement with reported values in literature [58, 59]. This is known to be due to an electronic activated behavior associated with the semiconductor bandgap. We suspect that the steep rise in the conductivity for $T > 417$ K is a direct consequence of measuring in a temperature range close to the phase transition temperature ($T_{\alpha\beta} = 451$ K). This transition is the so-called order-disorder transition when the electronic and ionic conductivity increase by several orders of magnitude [26]. The measured conductivities agree with conductivity values reported in literature by Bonnacaze et al. [25] and Miyatani [58], confirming the semiconductor properties of the fabricated α - Ag_2S thin films.

3.4 Electrical Switching

Electrical measurements of switching were performed perpendicularly across the Ag_2S layer, using a two-probe configuration. A Pt film is used as the bottom electrode and a micrometer-scale probe contact (a Pt or Ag wire, 0.1mm diameter) as the top electrode, applied with a small mechanical load. A diagram of the electrode configuration is shown in Fig. 3.3. A bias voltage V_b is applied to the Pt bottom electrode and the current is measured between the top electrode

on the Ag₂S film and ground. All experiments were done at room temperature and under atmospheric pressure.

3.4.1 I-V characteristics

Current- voltage (IV) curves were obtained by continuously sweeping the voltage from $0 \rightarrow V_{max} \rightarrow 0 \rightarrow -V_{max} \rightarrow 0$, where V_{max} is the maximum applied bias voltage. We present a summary of the measurements in Fig. 3.3, which features six values of V_{max} (200, 250, 350, 450, 550 and 700 mV, respectively). At low bias voltages, $V_{max} = 200\text{mV}$ (Fig. 3.3a), the device presents a rectifying characteristic. We define this behavior as the pre-switching state: Ag₂S presents semiconductor properties and no hysteresis is observed in the IV curves. The shape of this IV curve and the steady state behavior (pre-switching) will be described in detail in Chapter 4.

At $V_b > 200$ mV (Fig. 3.3b, c and d), the asymmetry of the IV curves remains, but in addition we observe hysteresis, starting at positive bias voltages. Upon increasing the bias voltage range, this hysteresis evolves into full bipolar switching (see Fig. 3.3e and f). In this case, the ‘on’ and ‘off’ states of the device are clearly observed. Following the arrows in the IV curve (Fig. 3.3f), a clear jump in the current is observed when a positive voltage is applied to the Pt bottom electrode (curve section ‘1’). The current increases, reaching values in the mA range at V_{max} , which represents the ‘on’ state. Sweeping back the voltage (curve section ‘2’), the ‘on’ state persists even at moderate negative voltages. When a sufficiently high negative voltage is reached, we observe a sudden decrease in the absolute value of the current. We define this as the switching of the device to the ‘off’ state (curve section ‘3’). The device remains in the ‘off’ state until a positive voltage switches the device back to the ‘on’ state. The polarity for switching is imposed by the geometry of the electrodes, a micro-scale top contact and a large bottom electrode, as shown in the diagram at the top of Fig. 3.3.

Upon calculating the resistance in the ‘on’ state of Fig. 3.3f, we find values from 90 to 125 Ω . This high metallic conductance property of Ag₂S films after switching has been reported in the literature [14, 23, 60]. In these reports the linear IV curves are interpreted as being due to the formation of a metallic filament which grows due to ionic transport and the subsequent reduction of the Ag⁺-ions at the negative electrode. A metallic Ag filament will then form connecting the

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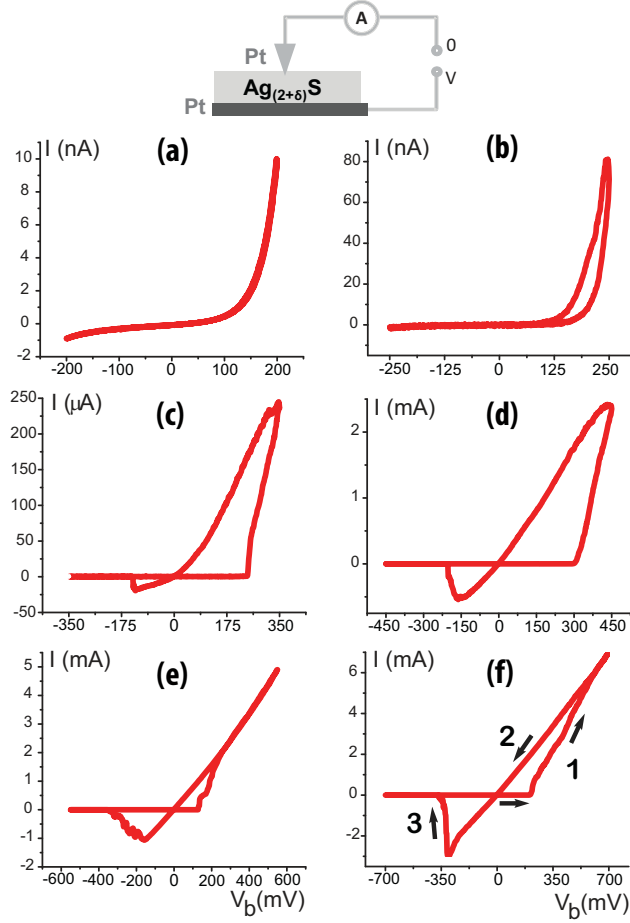


Figure 3.3: Top: Electrode configuration for electrical measurements of switching behaviour. The top electrode is a Ag wire. (a-f) Current- voltage characteristics of the device for different bias voltage ranges ($V_{max} = 200, 250, 350, 450, 550$ and 700 mV, respectively).

electrodes and turning the switch ‘on’. Switching ‘off’ is achieved by changing the polarity of the bias voltage, causing the metal atoms to oxidize and dissolve, annihilating the filament. Although the picture of redox processes at the electrodes is widely accepted, in the case of Ag_2S , the interpretation of the switching mechanism is not consistent in the reported literature. In many cases, the high conductance is attributed to a Ag metallic wire which bridges a tunneling gap between the surface of the Ag_2S and a Pt electrode, claiming that Ag_2S is an electrode with resistance of $\approx 100 \Omega$ [23, 49, 61]. In other articles, the same group attributed the high conductance to a Ag metallic filament growing inside

the Ag_2S film [46, 60, 62]. Because Ag_2S is a high resistive material, we believe that the metallic filament should grow inside the film (even in the presence of a tunneling gap (See Chapter 5)) to reach resistance values of 90Ω .

Following the idea of the formation of a conductive filament, we can interpret our IV measurements as follows. Initially, and as long as the Ag_2S is not decomposed, only the semiconductor behavior is observed. When the applied electrical potential is higher than a threshold voltage, the Ag_2S decomposes and elemental silver starts forming at the cathode (the micro-electrode) [63]. The metallic Ag starts accumulating at the boundary and grows towards the anode (the large bottom electrode). The filamentary growth of the deposited Ag can be explained as the result of the field pattern formed between the electrodes (Fig. 3.4). Furthermore, irregularities on the deposited metal enhanced the electric field and thus the flux of Ag ions is onto their tips. Consequently, the distance between the growth front and the anode is reduced enhancing the field even more, and causing the tip to move faster than the surrounding metal front. Finally this tip connects the bottom electrode shorting the device. The hysteresis in Fig. 3.3b is a result of the relatively low bias applied. Hence, the effective switching time is much longer than the inverse frequency of the IV measurement ($f = 1\text{Hz}$). At higher biases, the driving force on the ions will be larger, so that switching will be faster. We will elaborate on this below.

When sweeping the voltage over multiple cycles, we also observed a change in the IV curves from the first to the following runs, i.e. a memory effect in the sample. In Fig. 3.5 the first IV curve (orange curve) presents a higher switching voltage and lower conductance than all later curves, while the last curves present the lowest switching voltage and higher conductance. In the framework of the model discussed above, we propose the following interpretation. When the device is switched ‘on’ from its virgin state, it is possible that a lattice modification occurs, accompanying the filament growth. When the device is switched back ‘off’, the lattice does not return to its initial state, and the accumulation of ions at the negative electrode will not be completely undone. This supports the assumption that permanent changes occur in the sample when mass transport of ions initiates. In Chapter 6 this topic will be further discussed.

To investigate the changes in conductance as a function of V_b as well as its time dependence, an additional experiment has been performed. Starting with

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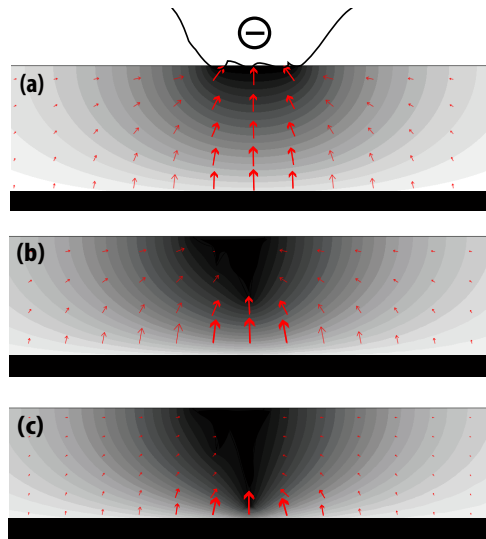


Figure 3.4: Simulation of the electric field lines (represented with the arrows) and the electrical potential (contour plot) across the Ag_2S layer when a voltage is applied between the two metals electrodes. The black bottom layer represents the large Pt electrode, and the Pt or Ag top contact wire is sketched at the top of (a). The metallic filament is also presented in black growing from the cathode towards the anode. In (b) and (c) the asymmetry of the Ag filament results from the possible irregularities in the metal deposited.

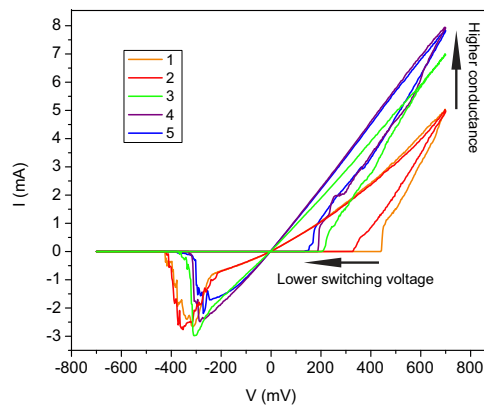


Figure 3.5: Multiple sweeping in voltage shows the changes (indicated by the black arrows) in the IV curves from the first curves with higher switching voltage and lower conductance (curves 1 and 2) to the last curves with lower switching voltage and higher conductance (curves 3, 4 and 5).

the device in the ‘off’ state, a positive voltage bias is applied to the bottom electrode by a step function (from 0V to V_b), and is kept constant until the device reaches its maximum value in conductance. We present the results in Fig. 3.6.

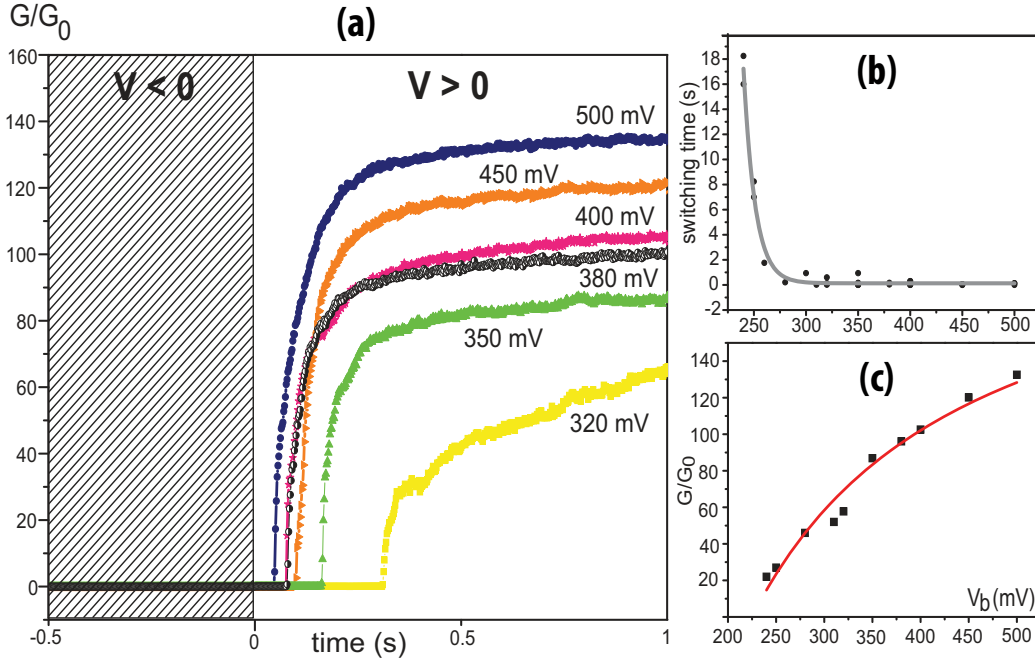


Figure 3.6: a) Increase in the conductance when a step function is applied to the device and keeping the voltage constant at its maximum amplitude, V_b (at $V < 320$ mV switching occurs at $t > 1$ s). b) Switching time as a function of the applied step voltage amplitude (V_b). c) Total conductance reached by the device as a function of V_b . The data points are in good agreement with a simple model, incorporating a series conductance $G_{series} = (233 \pm 10)G_0$ and a threshold voltage $V_{th} = 225 \pm 5$ mV (red curve).

Figure 3.6a presents the increase in conductance as a function of time. The switching time is defined here as the time at which the conductivity rises above $1G_0$, where $G_0 = 2e^2/h$. The time required to switch the device from the ‘off’ to the ‘on’ state depends strongly on the amplitude of the step in the voltage. At voltages from 200 to 275mV, it takes several seconds until the sudden rise in conductance is observed. This is consistent with the observation of hysteresis, i.e. incomplete switching, in the IV measurements of Fig. 3.3b, taken at $f = 1$ Hz.

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However, at $V_b > 275\text{mV}$, the switching occurs in less than a second. The dependence of the switching time with the applied voltage is presented in Fig. 3.6b.

When keeping the voltage constant, we observe after several seconds that the total conductance, G_{total} , reaches a maximum value and remains in this state until the applied voltage is changed. The measured saturation value of total conductance (expressed in multiples of the conductance quantum) increases with the applied voltage, as shown in Fig. 3.6c.

To understand this, we apply a model as follows. The conductance increases as a result of a combination of factors. In the interior of the Ag₂S film a conducting path is formed that consists of a metal filament and a modification of the local lattice of the material. The first of these two processes will continue as long as the applied voltage over the sample V_b is higher than a threshold voltage V_{th} . Assuming a fixed conductance for the external circuit, G_{series} , the voltage drop across the sample decreases as the sample conductance increases. As soon as this voltage drop is lower than V_{th} , the growth of the filament stops. Thus, for higher applied voltage, V_{th} will be reached at a higher conductance value, with a larger total cross section of the filaments formed.

We fit the experimental data in Fig. 3.6c with the equation for a voltage divider,

$$G_{total} = \left(1 - \frac{V_{th}}{V_b}\right) G_{series} \quad (3.1)$$

where $1/G_{total} = 1/G_{sample} + 1/G_{series}$ and V_{th} and G_{series} the fittings constants. As observed in Fig. 3.6c, the resulting curve (red curve in the plot) fits the experimental data very well. The value obtained for V_{th} is $(225 \pm 5)\text{mV}$ and for G_{series} is $(233 \pm 10) G_0$, which corresponds to a series resistance of $\approx 55 \Omega$. This series resistance can be largely attributed to the input impedance of the current amplifier. The value found for V_{th} is consistent with what we found from the IV characteristics of Fig. 3.3.

The calculated values of the sample conductance are within the range $24G_0 < G_{sample} < 307G_0$. This indicates that the final sample conductances, especially those corresponding to the higher applied voltages (450mV and 500mV), are already limited by the series conductance. Hence, in principle, by choosing a

proper V_b and G_{series} , the final sample conductance can be tuned and with it the filament formation in the device. The switching time, can also be regulated by the same parameters i.e. to obtain a lower switching time with the same G_{sample} , a higher V_b with lower G_{series} should be chosen. This principle was tested and is presented in Fig. 3.7. The Figure shows the measured conductance of the device, excluding the added series conductance. The measurements are performed after adding a series resistor of $4.3k\Omega$, and applying a step voltage from 0 (at $t=0s$) to 500, 700 and 800 mV. As expected, at voltages of 700 and 800 mV the device is switched on almost immediately, with times shorter than 10^{-5} s, where the measured time is limited by the sampling rate used. The sample conductances (G_{sample}) are only few units of G_0 and close to the values predicted using Eq.3.1, conductances much lower as compared with the conductances shown in Fig. 3.6a at $t = 0.5s$.

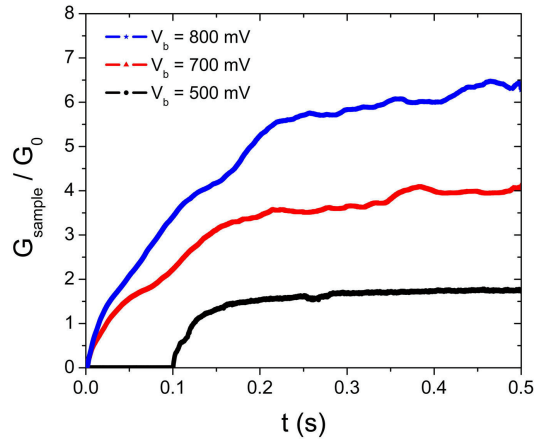


Figure 3.7: Increase in the conductance when a step function is applied to the device with voltage bias amplitudes of 500, 700 and 800mV. A series resistance of $4.3k\Omega$ is added to the measurement circuit. The sample conductance is calculated from the measured total conductance (G_{total}) and using $1/G_{sample} = 1/G_{total} - 1/G_{series}$

3.5 Conclusion

We have presented the electrical switching properties of Ag_2S thin films fabricated by sulfurization, and sandwiched between two asymmetric Pt electrodes. The electrical (IV) measurements enable the identification of an initial semicon-

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ductor behavior, followed by bipolar switching at higher bias voltages, when Ag₂S decomposes and a conductive path is formed. Bipolar resistance switching is observed during multiple cycles in all samples, provided that the applied voltage is higher than a threshold voltage V_{th} . The observed threshold voltage depends on the choice of electrode metals, and on the stoichiometry of Ag₂S. We will see in Chapter 4 that this value is significantly lower for a Ag bottom electrode, which provides a reservoir of Ag and fixes the chemical potential of Ag in Ag₂S. We show that the switching time and the final ‘on’-state conductance can be adjusted by choosing the series resistance and bias voltage properly. Understanding of the microscopic mechanism of switching is of great importance in order to optimize these systems for possible applications, e.g as ‘memristive’ devices [64].