Resistive switching in mixed conductors : Ag2S as a model system
Morales Masis, M.

Citation
Morales Masis, M. (2012, January 12). *Resistive switching in mixed conductors : Ag2S as a model system*. *Casimir PhD Series*. Retrieved from https://hdl.handle.net/1887/18364

6

Observing "Quantized" Conductance Steps in Silver Sulfide: Two Parallel Resistive Switching Mechanisms

We demonstrate that it is possible to distinguish two conductance switching mechanisms in silver sulfide devices at room temperature. Previously we show that in a metal/Ag_2S/metal device, the switch to a high conductance state is related with the formation of a conductive path between the electrodes. We argue this conductive path to be composed of a metallic silver nanowire accompanied by a modification of the surrounding lattice structure. Metallic silver nanowires decaying after applying a negative voltage allow observing conductance steps in the breaking traces characteristic for atomic-scale contacts, while the lattice structure deformation is revealed by gradual and continuously decreasing conductance traces.

J.J.T. Wagenaar, M. Morales-Masis and J. M. van Ruitenbeek, accepted for publication in J. Appl. Phys.

6.1 Introduction

Part of the interest in solid electrolyte memories, lies in the prospects to scale the devices down to few nanometers, and if possible to the atomic scale. Terabe et al. [23] reported atomic switching behavior by electrochemical reactions taking place in a vacuum gap between microfabricated Pt and Ag_2S electrodes. They showed switching between integer values of the unit of conductance, $G_0 = (12.9\ \mathrm{k}\Omega)^{-1}$, at room temperature and attributed this to the formation of a contact made up of few atoms. In a later report the decay with time of the high-conductance state was explored for implementing artificial synapses [61].

In the references above ([23, 61]), however, the presence of a vacuum gap is not supported by evidence, and one may argue that the assumption of the formation of a vacuum gap prior to the switching operation is unlikely. For the functioning of the device, the vacuum gap it is not needed because switching occurs inside the Ag_2S film, as commented in Chapter 3. Furthermore, in the previous chapter we demonstrated that control of the tip-sample distance requires biasing well below or well above the band gap when working with Ag_2S, therefore, the initial conductance of 1μS of the measurement in Ref.[61] is most likely for the STM tip in contact with the Ag_2S.

In this chapter we report on the conditions for observing such atomic switching behavior without a vacuum gap. We used a device composed of a thin film of Ag_2S deposited on top of a wide Ag layer, and the Ag_2S film is contacted with the Pt tip of a scanning tunneling microscope (STM). Applying a voltage between the electrodes leads to the reversible formation of a conductive path, defining the ‘on’ and ‘off’ states of the device. We analyzed the ‘on’ to ‘off’ conductance traces and found evidence for the coexistence of two parallel breaking mechanisms.

6.2 Experimental details

The samples are prepared as described in Chapter 2 Section 2.7. As the top electrode, we use an STM tip which is manually cut from a Pt wire. The measurements are performed in the JEOL UHV STM/AFM system. In this STM setup, the tunneling voltage is applied to the sample while the tip is connected to ground. The FEMTO (DLPCA-200) current amplifier is used to replace the standard JEOL current amplifier in order to cover a larger current amplification range. The measurements are performed at room temperature and at a pressure of 10^{-9}mbar.

6.3 Results

6.3.1 IV characteristics

Before starting the measurements we need to confirm that the tip is in contact with our sample. This can be decided based upon the measured current-voltage relation. When a large tunneling gap is formed the resistance is dominated by vacuum tunneling and the IV curve is nearly linear, for sufficiently low bias. On the other hand, when in contact an exponential current-voltage curve described by the expression derived in Chapter 4 is observed. The expression given by,

$$I(V) = K\sigma_0 \frac{k_B T}{e} \left(e^{(eV/k_B T)} - 1 \right) \tag{6.1}$$

with $\sigma_0 = 7.8\ 10^{-2}\ \Omega^{-1} m^{-1}$ the electronic conductivity of Ag_2S at zero bias [25], $T = 295$ K is the temperature, k_B is Boltzmann's constant, and K is a geometrical factor with dimensions of length representing the contact size.

We measured IV curves by ramping the bias voltage and measuring the current with a sampling rate of 10000 samples per second. In fitting the data with Eq. (6.1) K is the only fitting parameter, from which we determine the size of the Pt STM tip contact. Figure 6.1b presents the IV curve for the low-conductance state (off-state) and the fit of the curve to Eq. (6.1). From the quality of the fit we conclude that the sample is in its pristine, semiconducting, state and that the Pt tip is in contact with the sample. Increasing the voltage further causes switching to the on-state (Fig. 6.1a) due to the formation of a conductive path. Figure 6.1c shows an IV curve for the on-state, and the linear fit indicates metallic behavior. Subsequently, returning to a sufficiently large negative voltage the sample switches back to the off-state.

After switching the device several times the off-state conductance of the sample becomes strongly modified. The evolution of the off-state IV curves with the number of switching cycles is presented in Fig. 6.2. The switching cycles were

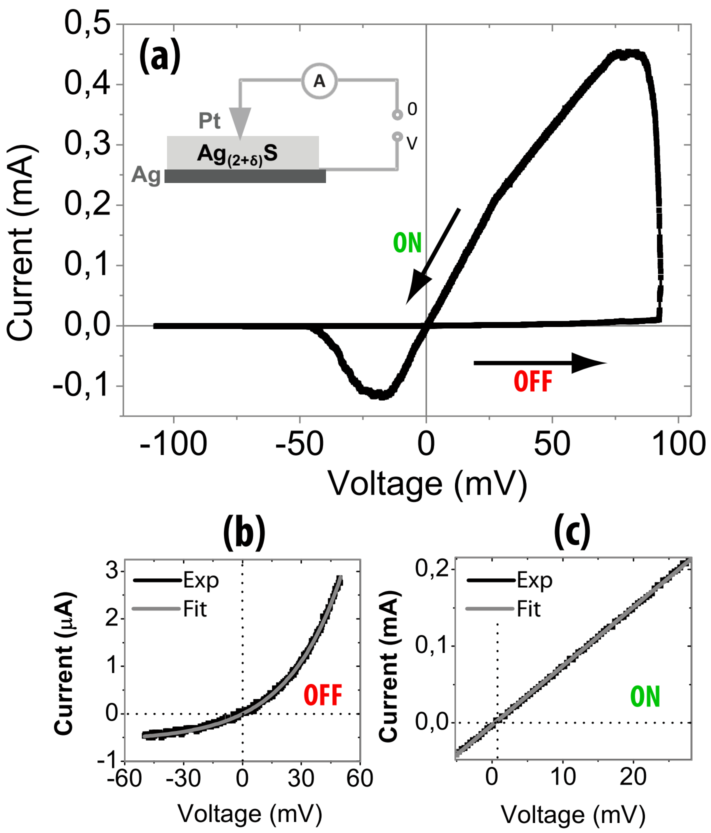

Figure 6.1: a) Current-voltage characteristics of a Ag/Ag$_2$S/Pt device (see inset) measured for a cycle duration of 1s. The ramp started at 0V and follows the arrows. In this IV curve full conductance switching is observed. The inset illustrates the contact geometry. b) Expanded scale view of the section of the IV curve in the 'off' state in (a). This part of the IV curve is fit very well by Eq. (6.1) (gray curve), indicating that the Pt tip is in contact with the Ag$_2$S film, and that the film is in its equilibrium (semiconducting) state. The zero-bias conductance of the off-state is approximately $0.2\mathrm{G}_0$ for this contact size. c) On-state section of the IV curve in (a). At this stage the sample has a conductance of $100G_0$, and the linear fit (gray line) indicates metallic behavior.

similar to the one shown in Fig. 6.1 and the IV curves were recorded a few seconds after every cycle. Starting from the IV characteristics of the pristine sample (green curve) we observed the conductance increasing from $0.1G_0$ to $1G_0$ after the sixth cycle.

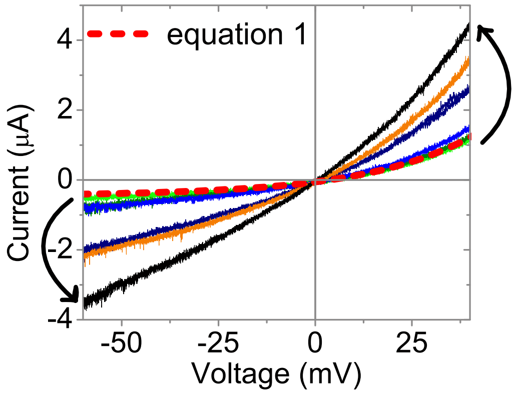

Figure 6.2: Evolution of the off-state conductance curve for a Ag_2S film with an increasing number of switching cycles. Each of the IV curves in the plot is measured after a full switching cycle, such as the one shown in Fig. 6.1a. The first curve (green) is measured after the first switching cycle, and the fit to Eq. (6.1) indicates that it remains close to the initial state of the pristine sample. The arrows give the direction of evolution for consecutive cycles. The zero-bias conductance of the junction changes from 0.1 G_0 (green curve) to approximately 1 G_0 (black curve).

Initially, the IV curves are described well by Eq. (6.1) (the red dashed curve). After several switching cycles the IV characteristic can only be fit by adding a significant linear term to Eq. (6.1). This changing sample conductance characteristics after switching has been reported previously and is referred to as the learning behavior of the switching mechanism [79], and is being explored for realizing artificial synapses [61].

6.3.2 Breaking

We measured traces of conductance as a function of time by control of the bias voltage in the following way: when the conductance was seen to fall below $0.5G_0$ a positive bias voltage was applied to the sample. To achieve rapid switching we used a voltage of +100mV. A high-conductance path was formed and the conductance was seen to rise to values above $100G_0$. Once G was detected to pass above $100G_0$ a negative bias voltage of −100mV was applied to the sample in order to break the conductive path, until the conductance approached the initial state of $G < 0.5G_0$. In this way the formation and breaking process is more controllable than by applying fixed pulses to the sample.

We measured many breaking traces at different spots on the sample and we recognized two types of traces: traces having a step-like pattern, and traces showing only a slow and continuous decay of the conductance. The observed patterns in the traces indicate the coexistence of two switching mechanisms.

The first mechanism is the dissolution of a metallic silver conductance path showing, at the final stages of the breaking, atomic conductance steps. When a metallic silver filament dominates the conductance, upon applying a negative voltage the filament at its weakest point will become reduced to only a few bridging atoms. In this way quantum properties of the conductance of the silver filament will show up [19]. Figure 6.3 shows some examples of atomic conductance steps observed in conductance traces recorded as a function of the breaking time. In Fig. 6.3a one observes that the conductance decays almost linearly until arriving at about $5G_0$, when steps of close to $1G_0$ in height start to be visible. Very pronounced plateaus and steps of approximately $1G_0$ can also be seen in the plots of Fig. 6.3(b), with a very long plateau of 0.4s in the middle trace. The upper trace also shows two level fluctuations with an amplitude close to $1G_0$ that is typical for atomic-scale contacts [19].

In an earlier series of measurements using a wire top-contact, we also observed steps in the breaking traces of conductance in a Ag/Ag_2S device cooled down to 220K. Two examples are presented in Fig. 6.4. The well defined step pattern, with the steps height close to 1 G_0, supports the assumption that, when the Ag filament is at the last stage of breaking and the weakest point is reduced to few atoms, atomic conductance steps are visible. The plateaus are longer than the ones observed in the traces measured at room temperature, which is expected due to the sample temperature of 220K.

However, there appears to be a second mechanism active. We conclude this from the observation of a slower and nearly continuous decrease of the conductance. Traces with atomic conductance steps at room temperature appeared only when the conductance rapidly dropped below $0.5G_0$ in approximately one second. When the decrease in the conductance was slower, we observed behavior as illustrated by the upper trace in Fig. 6.5. This is accompanied by a change in the IV characteristics similar to Fig. 6.2. We attribute this behavior to a second mechanism, most likely due to a modification of the local lattice structure giving rise to a region of increased conductance. This modification is probably induced

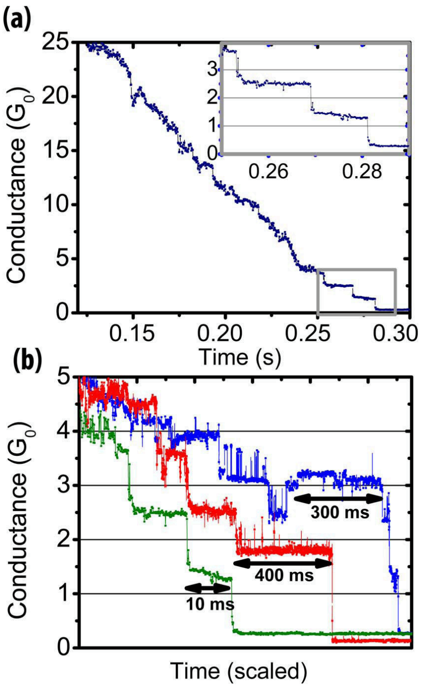

Figure 6.3: Steps in the conductance become visible when breaking the conductive path at a bias of -100mV. The conductive path was formed by applying a voltage of $+100$mV, allowing the conductance to reach $100G_0$ within a second. a) Breaking trace with three clear conductance steps of approximately $1G_0$ observed at the last stages of breaking. The inset shows a zoom of the steps. b) Three breaking traces with atomic conductance steps having different lengths in time. The measurements were performed on different spots of the sample and using different Pt-tips. The upper trace shows two-level fluctuations that are typical for atomic size contacts, and are attributed to single atoms oscillating near the contact.

by the electric field and the increased concentration of silver in the region of switching. It has been previously shown that the electric field can induced phase transitions, or decrease the phase transition temperature in materials like vanadium dioxide [80] and complex perovskites [81]. After applying a negative voltage silver diffuses back to the Ag bottom reservoir and the lattice slowly relaxes to its equilibrium structure.

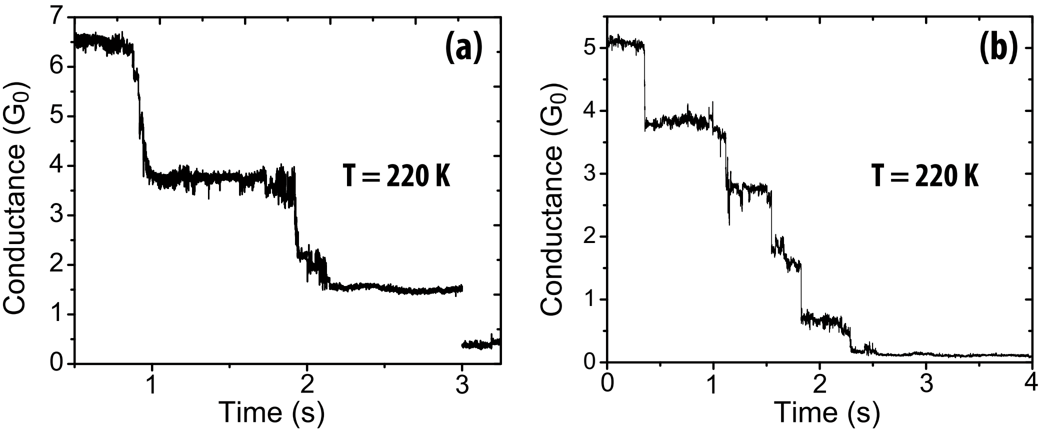

Figure 6.4: Steps in the conductance observed at 220K when breaking the conductive path at a bias of −100mV. The breaking traces show clear conductance steps of approximately $1G_0$ at the last stages of breaking.

Occasionally the two processes can be observed together, as illustrated in the middle trace in Fig.6.5: around $6G_0$ atomic conductance steps are visible, while somewhat later there is a continuous decrease over five seconds from 2 to $1G_0$. In terms of the two mechanisms described above this may be explained as being due to two parallel conductance paths.

6.3.3 Controllable switching

The continuous evolution of the IV characteristics in Fig. 6.2 and the continuous 'on' to 'off' conductance traces suggest that the local structure of the Ag_2S film has been modified. The conductance in this state can be controlled by applying positive bias voltages smaller than the threshold voltage. The voltages can be chosen to obtain specific values of conductance as illustrated in Fig. 6.6. In this example the conductance of the contact at a bias of -110mV was 0.3 G_0, slightly higher than the conductance of the contact in the pristine state of 0.1 G_0.

This nanoscale resistive switch in the regime of the quantum of conductance should not be confused with an atomic scale switch. The steps that we attribute to intrinsic atomic scale structure ('quantization') are only short lived (Fig. 6.3), and the IV curves in this state are linear, so that the conductance does not depend on the bias voltage. By controlling the second mechanism of conductance

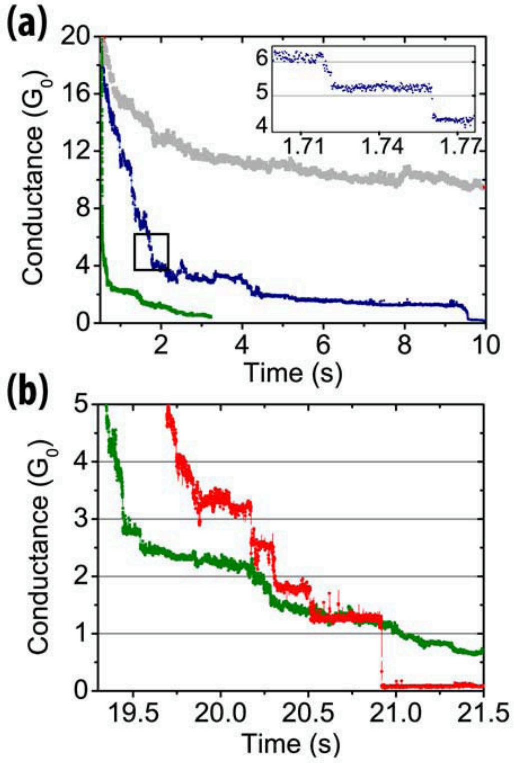

Figure 6.5: a) Continuous conductance changes observed when breaking a preformed conductive path at a bias voltage of -100mV. Mixed behavior is seen in the middle trace. The inset shows a magnification of the steps of approximately $1G_0$. The upper trace shows only continuous behavior and illustrates the high-conductance that is visible in some measurements after switching several times. The lower trace also shows only continuous behavior but the high-conductance state decays in few seconds to a conductance around $0.1G_0$. b) Comparison between a continuous trace (lower trace presented in (a)) and a trace with atomic conductance steps (red trace in Fig.6.3b)

switching any conductance, including ‘quantized’ values, can be set and maintained. The time scale for this process is much longer, and it allows manipulating the conductance over a wide range (Fig. 6.6).

6.4 Discussion

We have observed two types of conductance breaking traces, which we associate to the ocurrence of two switching mechanisms in Ag_2S. From previously performed experiments [19] we can state that a Ag atomic scale point contact presents steps

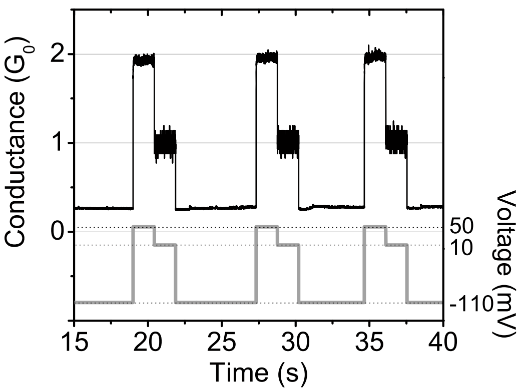

Figure 6.6: Switching between targeted values of conductance by applying specific low-bias voltages to the Ag_2S device. In this experiment the voltages were chosen such as to obtain approximately the first two integer conductance values, in analogy to the experiments by Terabe et al.[23]. Here we use fixed bias voltages instead of short pulses. This controllable switching can only be achieved after preparing the sample by several switching cycles. This example is chosen for illustration of the ambiguity that may arise when deciding whether a device is a true atomic scale switch.

in the conductance at the last stage before it breaks. However, the controllable switching, the continuously changing IV characteristics, and the gradually decreasing conductance traces cannot be explained by the formation of a metallic filament alone. The fact that the gradually decreasing conductance traces can take several seconds to return to the 'off' conductance (Fig.6.5), and decay of concentrations gradients in Ag_2S occurs much faster than a second [74] points towards the view that a modification of the lattice structure is induced, which we refer to as the second mechanism of conductance switching. Figure 6.7 shows a cartoon of the three different structures that may contribute in parallel to the total conductance: the pristine semiconducting sample (Ag_2S), metallic silver filaments (Ag), and the as yet undefined modified structure (X).

Our interpretation is consistent with the observations by Xu et al.[75] from *in situ* switching measurements of a Ag/Ag_2S/W device. From real time measurements inside a high resolution transmission electron microscope (HRTEM), Xu et al. determined that the conductive path formed when applying a positive voltage to the Ag electrode, is composed of a mixture of metallic Ag and argentite Ag_2S.

At room temperature, the equilibrium lattice structure of silver sulfide is the

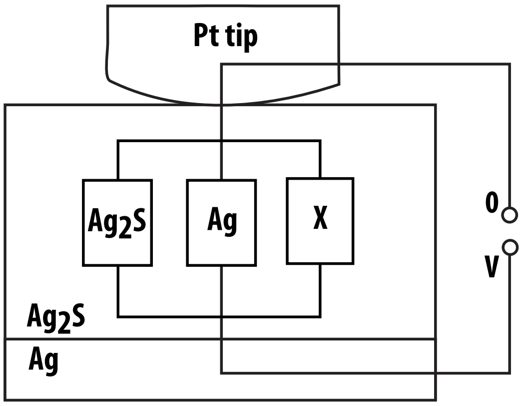

Figure 6.7: The measurements suggest that three structures are involved in the conductance after full resistive switching. Before switching we have our pristine sample which obeys the IV relation of Eq. (6.1). During switching a high-conductive path is formed by metallic silver and, in parallel, by a modified structure of the silver sulfide (X). An interpretation of this modified structure comes from comparison of our results with Xu et al.[75], who identified it in HRTEM studies as the argentite phase of silver sulfide.

so called acanthite phase. Above 450 K, the lattice undergoes a phase transition to the argentite structure. Argentite has an electronic conductivity that is three orders of magnitude higher, and behaves like a metal [29]. The argentite structure has previously been stabilized at room temperature by rapidly cooling of silver sulfide from high temperatures [46]. According to Xu's interpretation this phase transition to the argentite phase is not caused by Joule heating because the currents are quite low at the off state, but is believed to be driven by the increased silver ion concentration and the applied field.

Adhering to this interpretation of the phase transition we explain the observed continuous traces and mixed traces shown in Fig.6.5 as follows. The bias voltage drives both switching mechanisms: metallic filament formation and the local partial phase transition. When a silver filament is formed that stretches fully across the thickness of the film its high conductance dominates the observed electron transport. Break down of the filament at the last stages produces a connection formed by just a few atoms, and when these disconnect one by one this becomes visible as near-quantized steps in the conductance. When the metallic silver of a filament dissolves very rapidly or an incomplete filament is formed, atomic conductance steps will be absent and the conductance will drop continuously, as a result of the gradual decay of the locally modified structure. When the breaking of the silver filament occurs on the same time scale as the decay of the modified structure back to the initial room temperature phase, mixed behavior as seen in the middle curve in Fig. 6.5 can be observed. The conditions for the formation of a metallic silver filament and the observation of atomic conductance steps are not yet fully understood, since the two processes are controlled by the same bias voltage.

6.5 Conclusion

In summary, we identify two mechanisms of conductive path formation inside a thin film of silver sulfide. The first mechanism is the formation of a metallic silver filament which we associate with the observation of atomic conductance steps. Second, there is a modification of the silver sulfide structure to a higher-conductance phase. The conductance of this modified structure is continuously tunable, and allows setting the conductance to any target value by applying appropriate positive voltages. Contrary to previous reports [23, 61], we argue that this controllable switching cannot be attributed to an intrinsic atomic scale structure. The memory functions explored by Ohno et al.[61] cannot be explained by a metallic filament formation alone. Our results point towards the role of the two switching mechanisms in deciding whether the information is maintained for shorter or longer times.