Resistive switching in mixed conductors : Ag2S as a model system

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Summary

Non-volatile memories, computer memories that store information even when the power is off, are becoming increasingly important in information technology. The most common non-volatile memories used nowadays are flash memories, present in the memory cards of our cellphones, cameras and USB flash drives for example. With the appearance of new technologies there is a large demand for small, light and high capacity storage non-volatile memories. However, these memories are now reaching the miniaturization limits. The reason why there is a miniaturization limit, is because these memories store information by accumulating charge in memory cells * . The smaller these memory cells become the less charge can be accumulated and the less reliably the data storage. Because of this, new memory concepts are being investigated nowadays.

One proposed new memory concept is based on resistance switching, where data is stored as well defined resistance states on a material and not by accumulating charges. The resistance of a material determines how easy a material allows the passage of electrical current. Resistance switching is the change of the electrical properties of a material between two states, one state that allows the passage of current (low resistance state) and one state that prevents the passage of current (high resistance state). In terms of the memory concept, the low resistance state is called 'on' state (or 1) and the high resistance state is called 'off' state (or 0).

There are different mechanisms by which a material can change its resistance state. For example, a transformation of the crystal structure of the material, or the movement of atoms inside the material forming conducting paths. In this thesis I focus on the study of resistance switching due to movements of atoms inside a material and the reversible formation of a conductive path. These 'proof-of-concept' memories are also called 'Conductive-Bridge Memories'.

The Conductive Bridge memories are composed of two metal electrodes and a resistive material between then. Applying a voltage between the electrodes, induces a

*A memory cell is where one bit (a 0 or 1 in a binary language) of data can be stored

change in resistance, caused by the reversible formation of a conductive bridge. The formation or dissolution of the conductive bridge depends on the polarity of the voltage applied. The presence or absence of the conductive path forms the low and high resistance states respectively. Figure 7.1 presents a schematic diagram of the conductive bridge resistance switching concept.

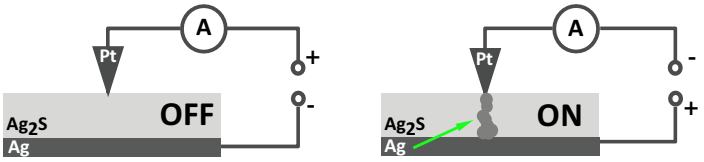

Figure 7.1: Schematic diagram of resistance switching in Ag_2S

The schematic diagram also represents the system studied in this thesis. In our experiments a silver (Ag) thin film is the bottom electrode, the middle layer is silver sulfide (Ag_2S), and the top electrode is a platinum (Pt) micro (10^{-6}) or nano(10^{-9})-scale contact. To create such a small top contact we used an atomic force microscope tip coated with platinum (Pt) or a scanning electron microscope (STM) Pt tip.

Silver Sulfide, Ag_2S, is a mixed conductor material, which means that its total conductivity is due to the motion of both Ag^+-ions and electrons. Mixed conductors are special materials because of their dual conductivity (ionic and electronic). In comparison, the conductivity of metals is only due to electron transport. The ion transport property of mixed conductors is the key ingredient for the conductive bridge memory presented in this thesis. Ions can easily move due to the applied electric field created by the voltage, and can form a conductive bridge between the top to bottom electrode. Once the bridge reaches from top to bottom electrode, the mixed conductor is short circuited, and the resistance drops. When the electric field is reversed (change in polarity of the voltage), the ions can move back to their 'original' position, the bridge breaks and the resistance increases again.

As with the $Ag/Ag_2S/Pt$ switching device, several other material combinations have been tested and demonstrated in literature as resistance switches, that work under the conductive bridge concept. The large interest in this research subject comes with the possibility to create a switch where only few atoms need to be moved to connect and disconnect the electrodes. This would mean scalability of the memory cell to a few nanometers (10^{-9}m) in size. In 2005, the research group led by Prof. M. Aono at

NIMS-Japan, reported the creation of an 'atomic switch' with a Ag_2S device. In their publication they claimed that the 'on' and 'off' states of conductance were due to the formation of a metallic filament composed of only a few atoms.

Although many of the points above sound fascinating, little has been explained in literature about the physical processes that drive resistance switching. Many details about the microscopic processes occurring before, during and after switching are unknown. For our research we aimed at understanding the mechanisms that drive resistance switching, and we focused less on device development. Understanding the fundamentals of the switching, helps for future development of the field, to make material choices when designing the memories, as well as to evaluate the true possibilities for future development of this type of memories.

The study of resistive switching in Ag_2S is presented in this thesis as follows. In Chapter 1 we describe the physical properties of Ag_2S. The semiconductor properties, crystal structure and the main phases at which Ag_2S can exist. In Chapter 2 we present the two fabrication methods we used to grow our samples, the advantages and disadvantages of each method and the characterization of the Ag_2S devices.

In Chapter 3 we present measurements of resistance switching in Ag_2S devices. We apply a voltage ramp to the device in the direction from 0V to V_{max}, then from V_{max} to -V_{max} and then back to 0V, and measure the response of the current. We present this in so-called IV-curves. We performed IV-curve measurements with different voltage amplitudes (V_{max}) and we observed a change in the shape of the IV curves with increasing V_{max}. The most notable change is that above a certain voltage, the IV-curves show an open loop (also called hysteresis), indicating that the voltage induces changes in the sample, and therefore, the current response is different in the forward and backward direction of the voltage ramp. At the largest voltage tested, the IV-curve clearly shows semiconductor behavior and high resistance up until a certain voltage. At a certain voltage the behavior changes and the sample switches to metallic behavior and low resistance. This state remains like this until V_{max}. Then, upon lowering the voltage towards -V_{max} the metallic behavior remains until a certain negative voltage. There the sample switches back to a high resistance and semiconductor behavior. This demonstrates the so-called 'resistance switching'.

In Chapter 4 we study the processes before switching, i.e. the IV curves at very low voltages, where no hysteresis is observed. This type of IV curves represents the steady state, and defines the pre-switching state. An important result from this chapter is that not only the reduction of the Ag^+-ions ($Ag^+ + e^- \rightarrow Ag_{metal}$) at the Pt electrode is

important to start the switching, but that a supersaturation (increased concentration) of Ag at the region close to the Pt tip is necessary to nucleate the metallic Ag. This metallic Ag is what later forms the conductive bridge. We describe the switching in our Ag_2S devices as follows. The formation of the conductive path is induced by applying a voltage between the electrodes. The applied voltage creates an electric field across the Ag_2S, that causes a flux of Ag^+-ions and electrons. If the negative voltage is at the Pt electrode, the Ag^+-ions move towards the Pt tip and accumulate in the region near to the tip. When the accumulation of ions is large enough, metallic Ag starts to nucleate. Because of the strong field created near the nucleated Ag, a Ag filament grows towards the Ag electrode, finally connecting the electrodes. This is the switching 'on' process, when the Ag_2S changes from the 'high' resistance state to the 'low' resistance state.

The prerequisite of supersaturation for the nucleation of metallic Ag and further resistance switching is confirmed in Chapter 5. We also find in this chapter that the nucleation of Ag on the surface of the Ag_2S can occur at voltages much lower than the voltage require for switching inside the Ag_2S.

In Chapter 6 we study the switching off process. We find that the low resistance state in Ag_2S is not only due to the formation of a metallic filament (as commonly assumed in literature), but that there is also a modification (possibly a phase transition) of the Ag_2S lattice. This leads to two important conclusions. First, using a mixed conductor like Ag_2S, the formation of a single atom switch is very unlikely to be achievable. This is because it is not only the movement and positioning of Ag atoms forming a bridge which defines the low resistance state, but also the surrounding Ag_2S lattice which is modified. The local modification of the Ag_2S lattice contributes to the low resistance. It then becomes difficult to determine if the low resistance state is due to the metallic Ag wire or to the modified structure of the Ag_2S. Following this, the second conclusion is that we can measure the same values of resistance characteristic of an atomic switch. However, those values of resistance are not due to the presence of a metallic contact of a few atoms, but results from a local modification of the Ag_2S lattice. Comparing our results with the results published in 2005 of the 'atomic' switch, we believe that those results should be explained in a different way than just a few atoms switching.

Although we made a large step forward in understanding the resistance switching process, there are still many open questions about the possibilities for scalability and performance of the conductive bridge switches before they can be used in real memory devices.