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

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Discussion and Outlook

In this chapter, we present a summary and discussion of the research in Ag_2S. Furthermore, the scientific and technical challenges for the future of the conductive bridge memories are discussed.

7.1 Introduction

In this chapter we present a conclusive summary of the research performed with Ag_2S as a model system. In the first two sections we comment on the application of Ag_2S as a model system to study conductance switching, and as a prototype material for fabrication of conductive bridge memories (CB-RAM). In the third section, a brief description of the future challenges and approaches reported in literature for development of the CB-RAM's is presented.

7.2 Ag_2S as a model material to study conductance switching

In our research, we have used Ag_2S as a model system to study resistance switching in mixed conductors. Ag_2S has been studied previously and can be fabricated by relatively straightforward techniques (See Chapter 2).

Most processes described in this thesis are also valid for many other mixed conductor materials. For example this applies to the Hebb-Wagner formalism for transport under steady state, the requirement of a supersaturation of the cations before nucleation of the metal phase, and the presence of two parallel conductance switching mechanisms. All this makes Ag_2S a good model system.

The property that sets Ag_2S apart is the fact that, the formation of a space charge layer at the electrode-electrolyte interface is negligible in the case of Ag_2S, which is not necessarily the case in other mixed conductor materials. This is due to the high ionic defect concentration in Ag_2S. In general, the formation of a space charge layer occurs in solid electrolyte/metal interfaces, and this effect has a larger influence when working at the nanoscale. When reducing the solid electrolyte film thickness to a few tens of nanometers, the film could reach the dimensions of the space charge layer, and even an overlap of the depletion layers of both electrolyte/electrode interfaces can occur. In such a case, the bulk properties of the electrolyte are expected to change [83]. This is, therefore, an important distinction to consider when working with other mixed conductor materials, where the ion defect concentrations are much lower than in Ag_2S.

7.3 Ag_2S as a material for resistive memories

Although Ag_2S forms an appropriate model system to study the physics of switching, it presents disadvantages as a prototype material for memory devices. First, the fast diffusion of ions at room temperature in Ag_2S is a disadvantage in view of the short memory retention time associated with it. Second, the low writing voltage (threshold for switching), although an advantage in terms of low energy operation, is a disadvantage in the definition of the read voltage. The read voltage has to be significantly lower than the writing voltage, such that, when reading it does not change the state (resistance) of the device. However, as seen in the experiments presented in Chapter 6 Section 6.3.3, even very low voltages (10mV) can modify the resistance of the 'off' state of the device. Third, the modification of the sample after several switching cycles is a disadvantage in terms of endurance, i.e. the amount of switching cycles before failure. On a non-optimized sample the maximum number of switching cycles achieved with our Ag_2S devices was approximately 500. To compete with contemporary flash memories, the number of switching cycles should be larger than 10^7 [2].

7.4 Challenges for the future of conductive bridge memories

Several ideas have appeared in literature for the development of nanoionic memory devices that fulfill the requirements of retention, endurance and performance of typical memories. Most of the approaches are in the direction of materials innovation, not only for the resistive layer, but also for the active layer (supplying the metal ions) and counter electrode (the inert metal). The list of materials that can be used as the ion conducting layer has been rapidly growing in the last few years, to the point that it includes not only solid electrolytes but all kind of semiconducting and insulating oxide materials. A summary of reported material combinations used for the fabrication of CB-RAM's is given in Ref.[82].

A further requirement for the development of CB-RAM memories, is the potential for scalability of the memory cells. This is actually a great motivation for the research in CB-RAM. The high scalability is due to the possibilities to reduced the metal filament dimensions to only a few atoms in cross section, bridging across the resistive thin film. The vertical scalability then requires the electrodes and the resistive film to be only few nanometers thick, i.e. 5nm or less each. The lateral scalability will require the memory cell to be less than 20 nm in diameter, and that the memory cell will have a well defined switching area, where the metallic nanowire grows and shrinks. Advances in this direction have been reported in literature. One example is GeSe devices showing scalability to below 20nm, and no device degradation when scaling to those dimensions [84]. As mentioned in Chapter 1 of this thesis, the ultimate scaling will be that in which the metallic filament is composed on only a few atoms. If possible even down to a single atom. So far, only Terabe et al. [23] reported the fabrication of an atomic switch. However, we have shown that the operation mechanism differs from their interpretation and the reproducibility of the switch needs to be further investigated.

Finally, to create a working memory with high density storage, the individual memory cells must be integrated into cross-bar arrays. The cross bar arrays are sets of parallel bottom electrodes, and perpendicular top electrodes, with a resistive material between the electrodes at each cross point. Because many of the memory cells can be connected in a line by either of the electrodes, crosstalk can occur through neighboring cells. The integration of the memories into cross-bar arrays, requires the addition of components or adjustments in the design of the memories cells, this mainly to prevent crosstalk (also called sneak path currents [85]) and misreading of the memories. One approach to solve the sneak path problem would be to use a rectifier element in series with each of the cells. Thin film diodes have been proposed in the literature for use as rectifying elements in cross bar circuits [86]. Another interesting approach, reported by Linn et al.[85] consists of a complementary resistive switch (CRS) composed of two memory cells connected antiserially. The CRS prevents the occurrence of sneak path currents and opens the possibility for building large passive cross bar arrays.

The investigations of resistive switching devices and implementation into cross bar arrays, have also led to new emerging ideas. For example, the synthesis of inorganic artificial synapses, with the prospect to build artificial neural networks. Two recent papers have shown the possibility to use the resistive switching memory cells as individual synapses. The first report uses a phase change memory cell as the synapse element [87], and the second report, uses a Ag_2S memory switch [61]. The short and long term memory of the synapses (also called plasticity) are determined by the conductances changes in the memory switch induced by voltage pulses. If the conductance decreases rapidly just after a weak voltage signal, it is called short term plasticity (STP). If the conductance remains for a long period of time after repeated strong voltage signals, it is called long-term plasticity (LTP). So far, the principle of artificial synapse has been shown only for individual memory cells, therefore, being no more than a concept implemented to the changes in conductance induced by voltage signals. However, the principle of artificial synapses is very attractive, and one can predict that several of the materials tested for resistive memories, will probably be tested for the fabrication of artificial synapses. Nonetheless, for a ‘real’ artificial neural network, reproducibility of the response to the voltage pulses, and to the operation of several synapses in a network is required. Finally, to match the complexity of the human brain, artificial neural networks need to contain around 10^{15} synapses [88].

7.5 Conclusion

Although several materials and memory cells are proposed in literature, the combination of all factors: performance, endurance, retention, scalability and integration into cross bar arrays, still need to be demonstrated for these memories. This leaves a wide set of open questions, materials and design issues to explore. Collaboration with several fields (chemistry, physics, electronics, materials science) is necessary for further investigations. Understanding the fundamental mechanism of switching is an important part of the research that will lead to a better design of the memory devices.

Appendix A

In Chapters 3, 4 and 5 we mention the presence of a threshold voltage above which nucleation and growth of a metallic phase inside the Ag_2S film occurs, leading up to conductance switching. Although it has been called a threshold voltage, it has not yet been clarified whether the switching is governed strictly by the bias voltage alone, or by the electric field that it causes. Specifically, it remains unclear what the rate determining process for conductance switching is.

The main observations from the chapters regarding the threshold voltage for conductance switching are as follows:

In Chapter 3, we find a threshold voltage of 225 mV in a device with the configuration Pt (bottom electrode)/Ag_2S/Pt (micro-wire), where the Ag_2S is at the stoichiometric composition. In Fig.3.5 of the same chapter, we also show that after multiple cycles, the voltage at which the switching occurs is reduced to approximately 100 mV.

In Chapter 4, we find a threshold voltage for switching above 70mV, in a device with the configuration Ag (bottom electrode)/Ag_2S/Pt (micro-wire and nano-contact). Here the Ag_2S is at the maximum stoichiometry in equilibrium with Ag. This threshold voltage did not show a significant change after several switching cycles.

Next, in Chapter 5, we confirm the 70 mV threshold voltage for Ag nucleation inside the Ag_2S film in the same device as Chapter 4. Additionally, we find that nucleation of Ag outside the Ag_2S film requires less than 20 mV.

The observation that for Ag_2S with lower Ag concentration ($\delta \approx 0$) the threshold voltage is larger than for the case of Ag_2S with maximum Ag concentration ($\delta = \delta_{max}$), indicates that the 225mV found for the first case, is related to the fact that initially, a local Ag ion accumulation is needed to reach supersaturation, at which the metal phase nucleates. This first step, involving ion migration is electric field driven. Once the Ag_2S film is locally modified, the threshold voltage is reduced to values close to the 70mV found in the case with $Ag_{2+\delta_{max}}S$.

The difference of the threshold voltage found for Ag_2S and $Ag_{2+\delta_{max}}S$, is comparable with values reported by Bonnecaze et al.[25]. Bonnecaze determined a potential larger than 105 mV to change the stoichiometry of $Ag_{2+\delta}S$ from $\delta = \delta_{max}$ to $\delta = 0$.

On the other hand, if the rate determining step is the charge transfer, the threshold voltage must be independent of concentration gradients, and the same threshold voltage for switching must be observed for both devices (with Ag or Pt bottom electrodes), which is not the case at least at the first switching cycles. Moreover, the fact that nucleation on the surface is possible at much lower voltages, below 20mV, points towards the conclusion that the rate determining step for conductance switching inside the Ag_2S is the nucleation of the new metal phase. Although, from the experiments performed we cannot fully exclude a field driven process, in view of the arguments above, we will rather tend to favor a voltage driven process, related with the nucleation of metallic Ag inside the Ag_2S.

Finally, it is important to mention that, whether the charge transfer, nucleation of the metal phase or slow diffusion under the influence of an electric field is the rate determining step, strongly depends on the memory resistive device, i.e. on the electrodes and the electrolyte material used [82].