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Resistive switching in mixed conductors : Ag₂S as a model system

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Introduction

In this first chapter, the motivation for this thesis is given. Historical background and the basic concepts of resistance switching in solid state memories are also presented. The second part of the chapter is dedicated to the introduction of our model material, Silver Sulfide. In the final section, general concepts of mixed conductors are also presented.

1.1 Introduction and Motivation

Since the invention of the transistor in 1947, the semiconductor industry has been looking for small, fast, high density storage and low power consumption memory devices. The ultimate memory device will be miniaturized down to few nanometers, requiring an ultimate downscaling of the active components to atomic scales.

Nonvolatile memories (NVM) are computer memories in which information is stored even when the power is off. One of the most commonly used type of NVM is Flash memory, which is found in solid state hard disks and memory cards used for digital cameras and cell phones. Although flash memory chips have reached downscaling sizes up to several tens of nanometers, they are now reaching the physical scaling limit, that is miniaturization of devices beyond 20nm [1].

To overcome this problem, in the past 10 years, new concepts have been introduced for the development of new NVM [1]. One of these new concepts is Resistance Switching, also known as Resistance Random Access Memories (RRAM). The concept is based on electrically switching the resistance of a material from high resistance (insulating behavior) to low resistance (metallic behavior) state, forming the 0s and 1s of stored digital data bits [2].

The concept of electrically switching the resistance of a material has been widely explored in the last few years. And with it a long list of materials that present resistance switching have been reported in literature [3]. The materials are in the family of insulators or semiconductors and the typical configuration of the system is a two terminal device of the form $M_1/X/M_2$, with X a resistive material sandwiched between the two metal electrodes M_1 and M_2 .

To switch the conductance of the resistive material in the two-terminal device $M_1/X/M_2$, a voltage above a certain threshold needs to be applied between the two metal electrodes. The switching in resistance is electrically induced in all cases, however, the physical process that causes the resistance switching is different depending on the resistive material 'X' used. These physical processes can be thermal, electronic, magnetic and ionic effects [1, 4]. In most of the cases the electrode material and asymmetry of the electrode configuration also play an important role.

Although resistance switching devices have been categorized according to the physical mechanism involved [4], many unsolved questions about the microscopic mechanisms, metallic nature of the on state, atomic arrangements at every switching cycle, switching reproducibility and many other detailed physical processes have not yet been elucidated.

Our contribution to this field, is to build a better understanding of the physical properties and processes involved before, during and after resistance switching in one specific case: when resistance switching is due to ion transport, and the ‘on’ and ‘off’ states are defined by the voltage induced reversible formation of a conductive path between the metal electrodes. Regarding this, our interest also lies in investigating the possibilities for reversible atomic wire formation.

All the different experiments performed in order to build this understanding are described in detail in this thesis. In this first chapter I will describe the basic principle of resistance switching in chalcogenide materials and the physical properties of our model material: Silver Sulfide (Ag_2S). In Chapter 2 I will present the fabrication techniques used to grow the Ag_2S thin films and deposition of electrodes, as well as the characterization techniques. Chapter 3 deals with the reversible conductance switching properties measured in Ag_2S films fabricated by sulfurization, and placed between Pt electrodes. Next, in Chapter 4 a quantitative analysis of transport in Ag_2S devices under steady state is presented. The Ag_2S films fabricated by reactive sputtering and placed between a Ag and a Pt electrode. In Chapter 5, STM measurements and conductance switching with the presence of a tunnel gap are presented. Chapter 6 demonstrates the presence of two conductance switching mechanisms in silver sulfide, from a study of conductance breaking traces. To conclude, Chapter 7 provides a summary and conclusive remarks from the presented chapters, and a discussion about the prospects of these “proof-of-concept” memories.

1.2 Resistance Switching in Chalcogenides

As mentioned in the introduction, several physical processes can be involved, individually or combined, in the process of resistance switching. I will focus on switching due to thermal and ionic effects, which typically occur in chalcogenide materials. Later in this thesis I will focus only on the switching due to ionic transport.

1.2.1 Chalcogenides

Chalcogenide materials are amorphous semiconductors composed of a chalcogen element from the group VIA of the periodic table: sulfur (S), selenium (Se) or tellurium (Te), excluding oxygen (O), and one or more electropositive elements: Au, Ag, Cu, Ge, Sb, Si among others. There are binary (Ge-Se, As-S, Ge-Te, Cu-S, Ag-S, Ag-Se), ternary (Ag-Ge-Se, Ge-Sb-Te, Ag-Sb-Te) and alloy chalcogenide compounds, and they exist in a wide range of atomic ratios and therefore present also a rich variety of electronic properties [4]. Another special property of solid chalcogenides is how the material properties can be easily modified by small changes in temperature, pressure, or other external parameters, like the application of a voltage [4, 5]. These unique properties make solid chalcogenides extremely interesting materials for electronic devices, in the fabrication of e.g. solar cells, fuel cells, batteries and memory devices.

Chalcogenide compounds with high ion mobility are also called solid electrolytes, examples of which are Cu and Ag chalcogenides (Ag_2S , AgGeSe , Cu_2S). Silver is especially appropriate for mass transport applications due to its ease of both reduction and oxidation and high mobility at room temperature [5]. The ionic mobility makes solid electrolytes interesting materials for the study of the effect of conductance switching as it will be further described in this chapter.

1.2.2 Resistance Switching

The concept of resistance switching in amorphous materials was first reported in the 1960's by Ovshinsky [6]. This report started a significant interest in materials that present a phase transition from amorphous to a crystalline phase. The phase transition causes a pronounced change of electrical and optical properties. This, together with reversibility of the process, are properties that have been widely studied for memory applications, e.g. NVM and optical rewritable media. Optical storage media have reached the level of commercialized products like compact disk (CD), digital versatile disk (DVD) and blu-ray disk (BD) [7].

Another resistance switching mechanism that was much later explored for possible application in non-volatile memories, is the reversible formation of conductive filaments across the solid electrolyte. This switching behavior was first reported in 1976 by Hirose and Hirose [8]. Using Ag-doped As_2S_3 as the resistive material, Hirose reported on the formation and annihilation of Ag dendrite as the

cause of resistance switching. The interest of this resistance switching concept, was later triggered in the 90's by Kozicki et al.[9]

These two concepts, phase change and conducting bridge memories, together with the valence exchange switching in transition oxide materials are the three main resistance-change memory concepts [10]. A brief description of these resistance switching processes is given below.

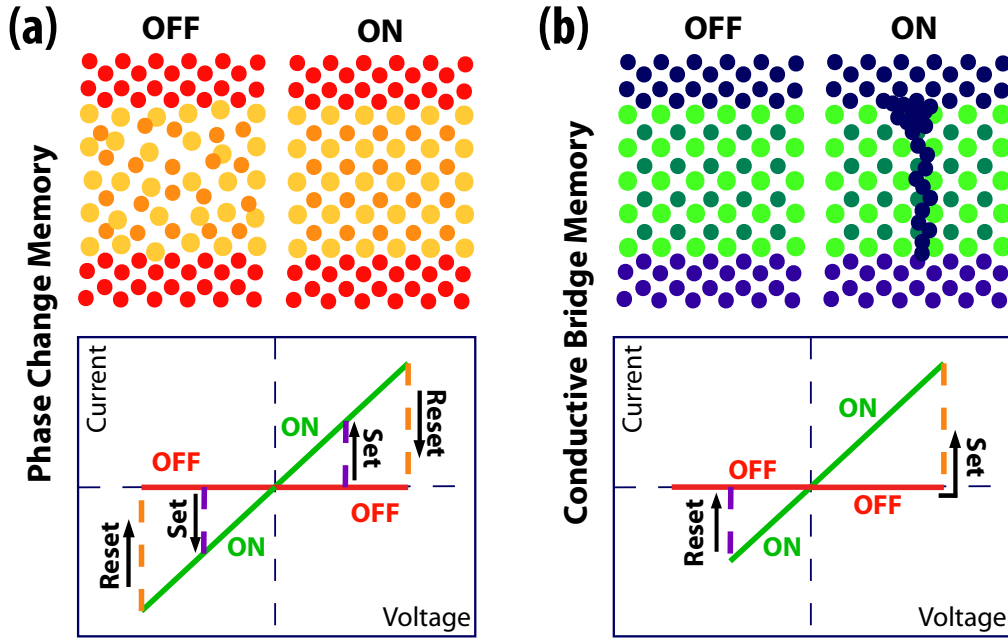


Figure 1.1: Schematic diagram of two switching processes. Current voltage characteristic of the switching and indication of the polarity dependence of the set and reset voltages.

Phase Change - based Resistance Switching

In phase change materials, the change from a disordered amorphous state to an ordered crystalline state causes a pronounced change in the resistance. The amorphous state has high resistance. When a voltage pulse is applied (a voltage above a threshold for switching), it locally heats the amorphous region causing recrystallization. The crystalline phase has low resistance. The application of a higher voltage pulse leads to local melting and the amorphous phase is formed again on rapid quenching. The system is then back to the high resistance state.

A representation of the transition from crystalline to amorphous is presented in Fig.1.1a. This switching mechanism presents unipolar switching, i.e. the set and reset voltages depend only on the amplitude of the voltage but not on the polarity. This is represented in the current-voltage characteristics of Fig.1.1a. Materials that show phase change switching are for example $\text{Ge}_2\text{Sb}_2\text{Te}_2$, Sb_2Te_3 , GeTe [11, 12].

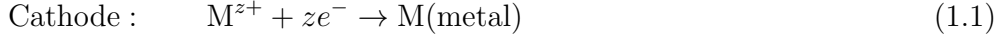
Phase Change materials are already being used in rewritable optical storage media and are probably the best candidates for future non-volatile memories. However, its use as non-volatile memories at low power operation and with high endurance, combined with scalability down to a few nanometers still present challenges [7, 10]. An extended review on this topic can be found in [7, 12, 13].

Conductive Bridge - based Resistance Switching

Also called electrochemical metalization cell (ECM), conductive bridge random access memories (CB-RAM) or programmable metalization cell (PMC) in the literature, as its name suggest, this memory concept is based on the reversible formation of metallic filaments inside a solid electrolyte lattice (Fig.1.1b) [14]. This is the type of memory that we have studied in this thesis.

The key ingredients in this type of memories are the mobile metal ions, a solid electrolyte as the ion conducting layer, an active electrode (A.E) working as the reservoir of the metal ions (e.g. Ag, Cu) and an inactive electrode (I.E) made of an inert metal (e.g. Pt, W). This switching mechanism presents bipolar switching, i.e. the set and reset voltages depend on the amplitude and polarity of the voltage applied. This is schematically represented in the current-voltage characteristics of Fig.1.1b.

The reversible switching process is commonly described as follows: initially the solid electrolyte has a large resistance, defined as the off state. When a sufficiently large voltage is applied between the electrodes, and when the negative polarity is applied at the inert electrode, the metal ions (M^{z+}) migrate towards the cathode and are reduced to metal atoms,



On the anode side (the active electrode) the metal atoms are oxidized to metal ions that dissolve into the electrolyte, maintaining the ion concentration in the electrolyte constant,



As long as the voltage is applied, ion migration in the electrolyte and further reduction of the ions, leads to the formation of a metallic filament that grows towards the anode. The first deposited metal enhances the electric field at its tip and this leads to the formation of a filament instead of a uniform deposition at the cathode. The metallic filament forms a conducting bridge between the electrodes, switching the device to the low resistance state ('on' state). When the voltage polarity is reversed, the metal atoms forming the filament will be dissolved back into the solid electrolyte and be deposited at the active electrode [2].

Figure 1.2 presents a typical current voltage characteristic of the switching and the corresponding diagram for each switching step.

There is a long list of materials that have shown this filamentary resistance switching concept [3]. The main requirement for the electrolyte is good cation conductivity, and one active electrode containing the cation (Ag, Cu). The solid electrolyte can contain the mobile metal ion in its composition (e.g. Ag_2S , Ag_2Se , Cu_2S) or host the foreign metal ions that are transported through the electrolyte from the active electrode to the cathode. In this case the electrolyte is a compound with high solubility of the active cation (e.g. Ag in GeSe) [2].

Oxide materials have also been used as the resistive layer in this type of memories. In this case two mechanisms can be distinguished according to the nature of the oxide layer and the contact material. The first mechanism is the same as the cation migration and reduction, forming and breaking a metallic filament inside the resistive layer. In this case the system consists of one active electrode (Ag, Cu), an oxide semiconductor that can work as the ion conducting lattice and an inert electrode (Pt, W). Some examples of these systems are Ag/ZnO:Mn/Pt

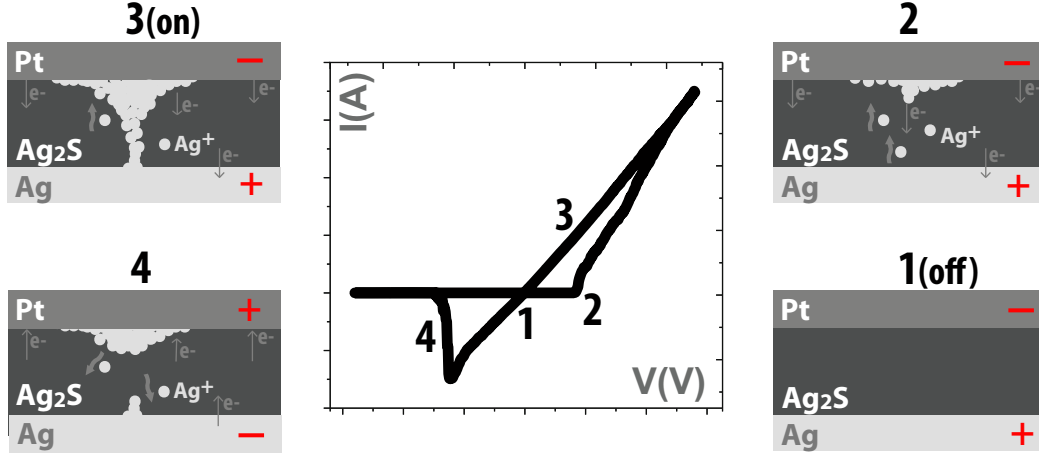
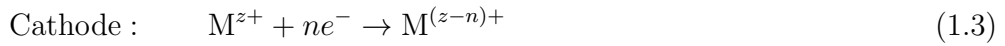


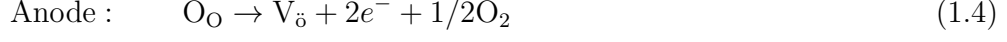
Figure 1.2: Current voltage characteristic of resistance switching caused by redox processes at the solid electrolyte-electrode interface [2]. The numbers from 1 to 4 indicate the order of the events.

[15] and Ag/Al₂O₃/Pt [16].

The second process has been defined as a valence change mechanism (VCM) by Waser et al.[4] and occurs in transition metal oxides or perovskites with at least one transition metal ion, when the oxygen vacancies have a higher mobility than the metal cations. The switching process is similar to the one described for the cation reduction, with the main difference that the mobile ions are oxygen vacancies. When a voltage is applied to the electrodes, the oxygen vacancies drift towards the cathode, and accumulate at the interface with the electrode. At the region where the oxygen vacancies accumulate, the valence of the transition metal is modified by the reduction reaction,



For example if the oxide is Ti₂O then $Ti^{4+} + ne^{-} \rightarrow Ti^{(4-n)+}$ [14]. The valence rich region grows towards the anode and forms a conducting path between the electrodes. The system is then in the on state. At the anode side, it is proposed that to compensate the cathodic reaction, the injection of vacancies into the electrolyte, written according to the Kröger-Vink notation, is given by



with O_O the oxygen ion in a regular site in the lattice, V_O the oxygen vacancies (double positive charge) and O_2 oxygen gas produced due to the oxidation reaction [14].

To switch the device to the low conductance state, the bias voltage is reversed and the vacancy rich filament is dissolved back and the system is back to the off state. The filamentary nature of the vacancy rich region at the on state has been demonstrated for the systems $\text{Pt}/\text{SrTiO}_3/\text{Pt}$ [17] and $\text{Pt}/\text{Ti}_2\text{O}/\text{Pt}$ [18].

The VCM process described is just one of many other switching processes observed in oxide materials, which are not covered in this thesis.

Fig.1.3 presents a classification of the proposed conducting bridge resistance switches, that work within the concept of redox reactions at the electrode interfaces.

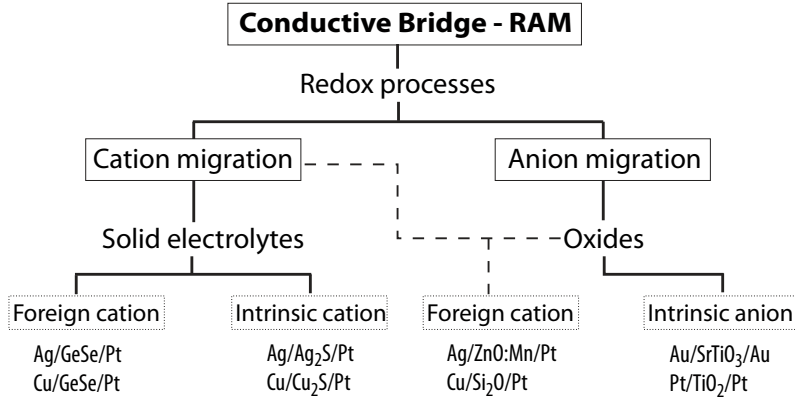


Figure 1.3: Classification of conducting bridge memories according to the type of mobile ions, electrode and resistive material. The examples of electrodes and resistive materials are written in the notation: active electrode/resistive material/inert electrode.

The resistance switching pictures explained above give just a rough description of the main physical processes widely accepted in the literature on resistance switching driven by redox reactions. However, there is a broad range of open questions about the electrochemical reactions on the electrodes, the ions involved in the process, the occurrence of more than one physical mechanism, the nature of the metallic state and many other that need to be solved before the conducting bridge concept can be implemented as solid state memories.

Atomic switches

The ultimate conductive bridge RAM, will be that in which the ‘on’ and ‘off’ states are defined by the addition and removal of a single atom, i.e. an atomic switch. When this is feasible, scaling of the switching devices down to few nanometers, low power consumption and ultra high speed operation would be possible.

Atomic-scale metallic point contacts have been broadly studied previously, and their technological prospects for their use, for example in transistors, is a motivation for the intense investigation. Metallic wires with a cross section area of few atoms lead to the appearance of quantum mechanical effects, and with it, quantization of the conductance in units of $1G_0 = 2e^2/h = 77\mu S$. For gold and silver, the conductance of a single atom is $1G_0$ [19].

Atomic switches have been fabricated in several ways. For example, three terminal gate-controlled atomic quantum switches, that can operate at room temperature, have been successfully developed by Xie et al.[20, 21] and Martin et al.[22] using different approaches. The first approach is the electrochemical deposition in liquid of Ag atoms between two large gold electrodes[20]. The number of Ag atoms in the quantum point contact were controlled with the potential of the gate electrode, allowing the reproducible switching of the contact between a quantized on state ($G = nG_0$, $n=0,1,2,3...5$) and insulating off state. The second approach consisted of a gated mechanically controllable break junction [22]. More specifically, a gold bridge with an atomic constriction suspended on top of a gate electrode. The electrostatic attraction between the source and drain electrodes leads to the reversible switching between a single atom contact ($G = 1G_0$) and tunneling regime.

In spite of these exciting results, indicating the possibility of individual atom manipulation for future atomic transistors, these switches still require special conditions to work (high vacuum), large setups (e.g. mechanical controllable break junctions) or liquid electrolytes that are difficult to implement in integrated circuits.

In 2005 Terabe *et al.* reported the reversible formation of Ag atomic contacts in the tunneling gap between the surface of a silver sulfide (Ag_2S) thin film and a Pt electrode. This was the first atomic switch proposed under the concept of conductive bridge random access memories (CB-RAM)[23]. The switching from low conductance (tunneling) to high conductance was induced by the applied bias between the Pt electrode and a Ag bottom electrode. The metallic Ag was formed by the reduction of Ag at the Pt electrode (negatively biased). To break the contact the polarity of the voltage is reversed and the Ag filament dissolves back into the Ag_2S layer. The ‘on’ and ‘off’ states of conductance were stable, and the authors presented the possibility to prepare the switch in well-defined quantized states of conductance, with $G = 0, 1G_0, 2G_0$ and $3G_0$, suggesting the possibility to realize a multilevel memory switch.

The interpretation presented, concerning the creation of an atomic switch, suggested that the metallic filament was formed on the surface of the Ag_2S , and that a tunneling gap is necessary to achieve a clear change in conductance from ‘on’ to ‘off’ states. However, we will argue that this interpretation cannot be valid, and we believe that the Ag metal filament formation takes place **inside** the Ag_2S layer, and that a tunnel gap is not necessary as the intrinsic conductance of silver sulfide is already very low.

The indications for the possible formation of atomic wires in an environment that will provide both mechanical stability and chemical protection, all under ambient conditions, is what motivated part of the work that is presented in this thesis. This also formed the trigger of many fundamental questions about the processes occurring in Ag_2S switches.

1.3 Ag_2S as the model system to study conduction switching effects

The material used for all the experiments described in this thesis is Silver Sulfide (Ag_2S). This dark gray colored material, which tarnishes silverware or silver objects over time, has called the attention of solid state scientists since the times of Faraday.

Silver Sulfide is a mixed conductor material, with a total conductivity due to the transport of, both, Ag^+ -ions and electrons. Silver sulfide presents good chemical stability and it exists in three stable phases, α , β and γ in order of increasing temperature [24]. Ag_2S corresponds to the family of the silver chalcogenides, which includes Ag_2Se and Ag_2Te . The structure of these materials is usually a rigid body-centered cubic (bcc) lattice, formed by covalently bonded chalcogen atoms. The Ag^+ -ions are distributed in octahedral and tetrahedral positions in the lattice. The number of octahedral and tetrahedral sites available is much larger than the number of Ag^+ -ions, and therefore there are always positions in the lattice available for the ions to move into. This results in a high ion mobility observed in all silver chalcogenides [5].

The physical properties of Ag_2S , i.e. electronic and ionic conductivity, crystal structure and distribution of defects, are strongly modified with temperature and composition (Ag/S ratio). Figure 1.4 presents the phase diagram of Ag_2S , indicating the stable range for each of the three phases as a function of temperature and stoichiometry parameter δ . The stoichiometry parameter δ indicates the excess ($\delta > 0$) or deficit ($\delta < 0$) of Ag in $\text{Ag}_{2+\delta}\text{S}$.

The low temperature phase ($\alpha\text{-Ag}_{2+\delta}\text{S}$), also called acanthite, is only stable within the narrowest range of non-stoichiometry (Fig.1.4b) with a composition range, δ_{max}^α , in the order of 10^{-6} [24, 25]. At 177°C , Ag_2S transforms to $\beta\text{-Ag}_{2+\delta}\text{S}$, the high temperature phase, also called argentite. The range of non-stoichiometry of the β -phase is much broader than the α phase (Fig.1.4a), with δ_{max}^β in the order of 10^{-3} [24, 26].

The formulation of the basic rules of solid state electrochemistry and its application to Ag_2S , were first given by Carl Wagner in the 1930's [27]. Since then, the most studied phase has been $\beta\text{-Ag}_{2+\delta}\text{S}$, due to its superionic properties. For

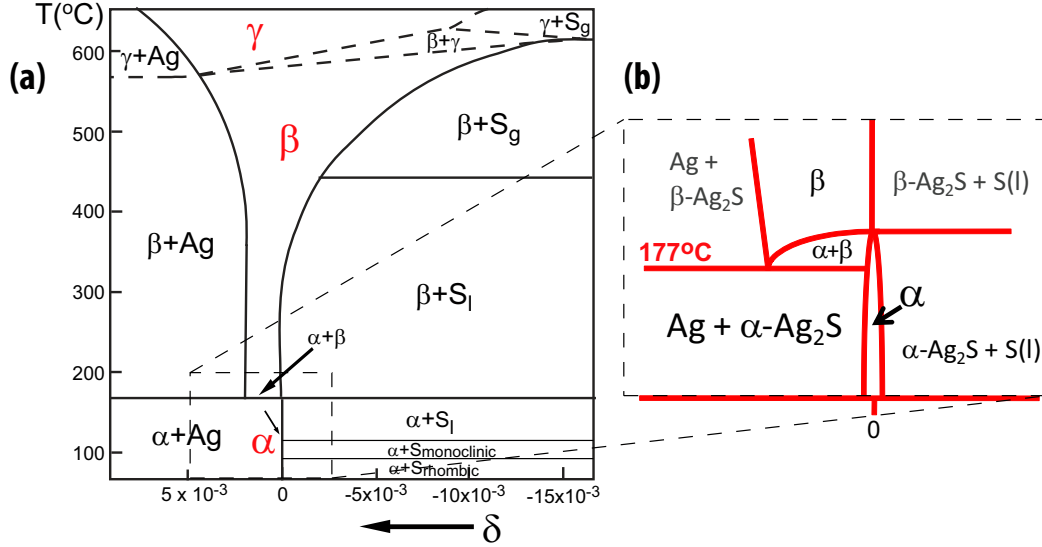


Figure 1.4: Phase diagram of the Ag-S binary system. a) The three phases of $\text{Ag}_{2+\delta}\text{S}$ are presented. Starting with $\alpha\text{-Ag}_{2+\delta}\text{S}$, the low temperature phase is stable from 0 to 177°C . At 177°C it transforms to $\beta\text{-Ag}_{2+\delta}\text{S}$ which is stable from 177°C up to around 590°C (depending on non-stoichiometry). Above 600°C , $\gamma\text{-Ag}_{2+\delta}\text{S}$ is the stable phase. Finally at above 840°C (not presented in the diagram) $\text{Ag}_{2+\delta}\text{S}$ is liquid. b) Zoom-in of the phase diagram at the α - β transition region. Data obtained from Ref.[24].

our purpose, the α phase is of special interest because it is the stable phase at room temperature. In the following section I will present the physical properties of the α and β phases, as reported in literature.

1.3.1 Crystal Structure

The crystal structure of the low temperature phase $\alpha\text{-Ag}_{2+\delta}\text{S}$ is monoclinic, space group $\text{P2}_1/\text{c}$, with $a = 4.231 \text{ \AA}$, $b = 6.930 \text{ \AA}$, $c = 9.526 \text{ \AA}$ and $\beta = 125.48^{\circ}$ [28]. This superstructure is composed of a slightly distorted body-centered cubic (bcc) lattice of sulfur atoms. The silver atoms are equally distributed in positions close to the tetrahedral and octahedral sites of the sulfur bcc array [29, 28]. Figure 1.5 presents the monoclinic structure of $\alpha\text{-Ag}_{2+\delta}\text{S}$.

At the high temperature phase, $\beta\text{-Ag}_{2+\delta}\text{S}$, the sulfur atoms form an ordered

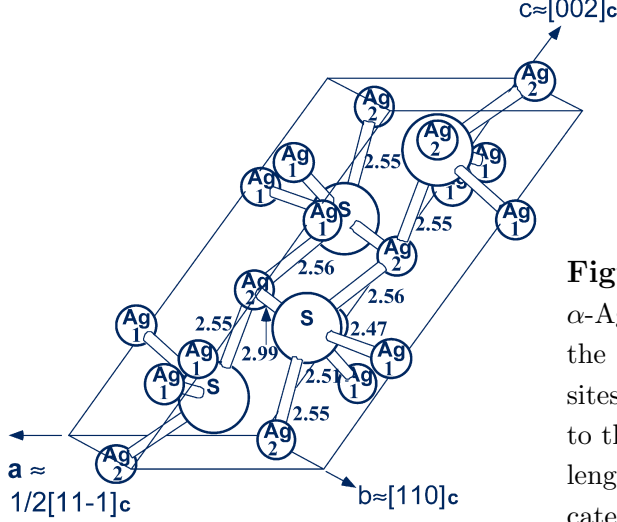


Figure 1.5: Crystal structure of $\alpha\text{-Ag}_{2+\delta}\text{S}$. In the figure, Ag(1) are the atoms close to the octahedral sites and Ag(2) are the atoms close to the tetrahedral sites. The bond length to the S atoms is also indicated. Reproduced from Ref.[29].

bcc lattice. The Ag atoms occupy the tetrahedral and octahedral sites in the lattice, with a higher occupancy of tetrahedral sites. Cava et al.[28] determined an occupancy ratio of 3:1 at the α - β phase transition, and an increase of the ratio with temperature up to 260°C when all the occupied sites are tetrahedral. The space group of $\beta\text{-Ag}_{2+\delta}\text{S}$ is the Im3m, with $a = 4.860 \text{ \AA}$ [24].

In summary, for both phases, $\text{Ag}_{2+\delta}\text{S}$ consist of a rigid immobile sulfur sub-lattice and a mobile Ag sub-lattice. The large mobility of the Ag^+ -ions in the lattice is due to the excess of octahedral and tetrahedral sites in the sulfur lattice as compared to the amount of silver in $\text{Ag}_{2+\delta}\text{S}$.

1.3.2 Electronic and Ionic Conductivity

As mentioned before, the total conductivity σ_t of Ag_2S is due to the simultaneous motion of both, Ag^+ -ions and electrons. Then, $\sigma_t = \sigma_e + \sigma_{\text{Ag}^+}$.

The temperature dependence of the total conductivity is presented in Fig.1.6. In the low temperature phase, $\alpha\text{-Ag}_{2+\delta}\text{S}$, the total conductivity increases exponentially with temperature, presenting semiconductor behavior. At the α to β phase transition, the ionic conductivity increases nearly two orders of magnitude, and the electronic conductivity nearly three orders of magnitude [29]. The conductivity in the β phase only varies slightly with temperature, presenting metallic

1.3. Ag_2S AS THE MODEL SYSTEM TO STUDY CONDUCTANCE SWITCHING EFFECTS

behavior. In both α and β phases, the total conductivity is strongly dependent on stoichiometry.

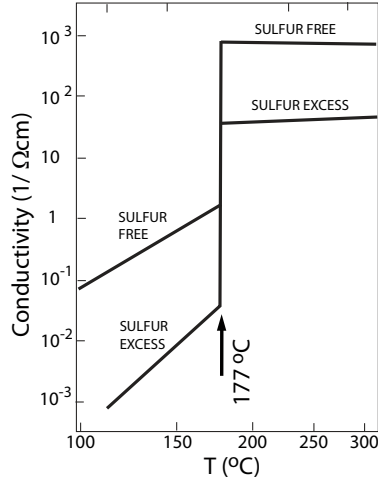


Figure 1.6: Electrical Conductivity ($\sigma_e + \sigma_{Ag^+}$) as a function of temperature. The pronounced change in the conductivity with the composition and phase transformation is clearly observed in the plot. The composition range presented shows the limits of silver sulfide in equilibrium with silver (sulfur free), and silver sulfide in equilibrium with sulfur (sulfur excess). Reproduced from Ref.[30].

Further research on the α phase demonstrated that $\alpha\text{-Ag}_{2+\delta}\text{S}$ is an n-type semiconductor, with a band gap ranging between 0.6 and 1.2 eV [26, 29, 31, 32].

In spite of the large number of reports on Ag_2S [29, 30, 33, 35], data on the electrical properties at room temperature are rare in literature. Bonnecaze et al.[25] published one of the few reports on the electrical properties of Ag_2S at temperatures ranging from room temperature up to 177°C, the phase transition. At room temperature, $\sigma_e \approx 7.8 \times 10^{-2} \Omega^{-1}\text{m}^{-1}$ and $\sigma_{Ag^+} \approx 3.4 \times 10^{-3} \Omega^{-1}\text{m}^{-1}$, which represents a contribution of 96% (σ_e) and 4% (σ_{Ag^+}) to the total conductivity (σ_t). The contribution of the electronic conductivity to the total conductivity is, in the low and high temperature phases, higher than the ionic contribution. However, at the high temperature phase, the ionic conductivity values are as high as those measured in purely ionic conductors (e.g. AgI) [24]. This is why $\beta\text{-Ag}_2\text{S}$ receives the name of superionic conductor.

The ionic conductivity is independent of composition or non-stoichiometry δ . This is explained to be due to the considerable freedom of the Ag^+ ions to move within several positions in the crystal lattice [30, 34]. Contrary to the ionic conductivity, the electronic conductivity is strongly dependent on non-stoichiometry (δ). Additional silver in silver sulfide acts as an n-type donor increasing the elec-

tronic conductivity. Then, as observed in the conductivity vs temperature plot (Fig.1.6), the increase of the total conductivity with additional silver is all due to the increase in the electronic conductivity.

The finding that the ionic conductivity is independent of the change on stoichiometry, led to the conclusion that α -Ag₂S has a majority of intrinsic thermal ionic defects, with these defects being of Frenkel-type [25].

1.4 Concepts and phenomenological transport equations of mixed conductors

In this section a brief background of defects and electrical transport in mixed conductors, as well as the phenomenological transport equations are presented.

1.4.1 Charge Carriers in Solids

The understanding of mixed charge transport and compositional variation in solids is possible using point defect chemistry, concepts that were developed in the 30's by Frenkel [37], Schottky and Wagner. Point defects are atomic size defects, and consist of vacant lattice sites, extra atoms in not regular lattice positions (also called interstitial positions) and chemical impurities. Higher dimension defects, like dislocations, grain boundaries, and voids are conglomerations of these point defects. Thus, ionic and electronic conductivity as well as diffusion processes, all depend on local deviations from the perfect crystal lattice, i.e. on the presence of point defects [36, 38]. The possible combinations of point defects in a crystal, following the principle of electric neutrality are presented in Fig1.7.

The most accepted notation for point defects is the so-called Kröger-Vink notation [38]. In a mixed conductor MX with cation Frenkel disorder, this notation indicates the elements of the structure as follows,

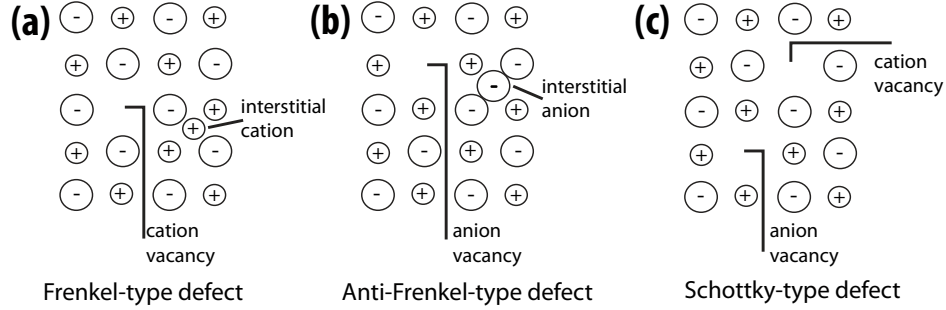


Figure 1.7: Types of point defects in a crystal. a) and b) Frenkel defect: combination of a vacancy and an interstitial ion. c) Schottky defect: a cation and an anion vacancy. Reproduced from [36].

- M_M Cation, M^+ , located on a regular site of the lattice (position represented with the subscript M).
- V_i Vacant interstitial site, a normal component of the ideal lattice.
- $M_i^\bullet$ Cation on interstitial site (subscript i) with a relative charge +1 (superscript $\bullet$)
- V_M' Vacancy at cation site with a relative charge -1.
- $e', h^\bullet$ Electron, hole and their respective charge.

The relative charge is the difference in charge at the defect site relative to the charge at the site of the perfect crystal (A dot for each extra positive charge or a slash for each extra negative charge) [38]. The Kröger-Vink notation is important in the definition of equilibrium reactions and deviations from stoichiometric compositions. This will be shown in Chapter 4.

1.4.2 Transport equations

The transport of charge carriers in mixed conductors is correctly described by the theory of irreversible thermodynamics. The theory relates the occurrence of fluxes (J_j) to perturbing forces (X_j) in a system. In an irreversible process, the rate of entropy production ($\dot{s} > 0$) is related with the flux and perturbing force as,

1. INTRODUCTION

$$\dot{s} = \frac{1}{T} \sum_{j=1}^n J_j \cdot X_j \quad (1.5)$$

with T the temperature.

The theory as developed by Onsager [39] states that as long as a force-flux relation can be expressed as in equation 1.5, the forces and their fluxes are linearly related. The linear relation is given by the Onsager theorem [39],

$$J_j = \sum_k^n L_{jk} X_k \quad (1.6)$$

with the coefficient L_{jk} independent of X_k . According to the Onsager theorem [39], in systems near equilibrium $L_{jk} = L_{kj}$.

The importance of these relations in the description of transport in mixed conductors, is that the linear macroscopic laws of transport (e.g. Ohm's law for conduction) are generalized, so they include cross-terms. These cross-terms represent all fluxes and forces, for example in case of more than one mobile species, it counts the interaction between the fluxes of the distinct species in the solid.

As an example, let's consider again the mixed conductor MX with mobile cations and electrons. In this case, there are two types of fluxes, the electron flux j_e and ion flux j_i . When these fluxes are induced by potential gradients, the forces can be written as,

$$X_e = \nabla \tilde{\mu}_e = \nabla \mu_e - e \nabla \phi \quad (1.7)$$

$$X_i = -\nabla \tilde{\mu}_i = -\nabla \mu_i + e \nabla \phi \quad (1.8)$$

and from equation 1.6,

$$j_e = \frac{\sigma_e}{e} \nabla \tilde{\mu}_e - \frac{\sigma_{ei}}{e} \nabla \tilde{\mu}_i \quad (1.9)$$

$$j_i = -\frac{\sigma_i}{e} \nabla \tilde{\mu}_i + \frac{\sigma_{ie}}{e} \nabla \tilde{\mu}_e \quad (1.10)$$

where j_e and j_i are the electronic and ionic current densities, and σ_e and σ_i are the conductivities. The conductivity is given by $\sigma = eZN\mu$, where N the concentration (cm^{-3}) and μ the mobility (cm^2/Vs). For some mixed conductors, the Onsager cross coefficients (σ_{ei} and σ_{ie}) are negligibly small compared with σ_e and σ_i [40, 41]. Therefore the cross-coefficients will usually be omitted in the treatment of silver chalcogenides with cation Frenkel disorder.

1.5 Conclusion

In this chapter we presented a new concept for memory devices, with the prospect to overcome the scalability limit of few nanometers of traditional, transistor based memories. This concept is based on Resistance Switching. Silver and Copper chalcogenides with high ionic mobility, are candidate materials investigated for the development of this type of memory devices. Silver Sulfide is one of these chalcogenides, and presents interesting properties as mixed conductivity, semiconducting properties and high ion mobility. These properties made Ag_2S attractive as our model system to investigate the fundamentals of switching in mixed conductor materials.

1. INTRODUCTION
