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Resistive switching in mixed conductors : Ag₂S as a model system

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Ag₂S: Fabrication and Characterization Techniques

This chapter describes two fabrication methods used for the growth of Ag₂S thin films. The specific growth parameters are presented for each method as well as the subsequent characterization of the thin films. The advantages and disadvantages of each method will also be presented in the chapter.

2.1 Introduction

In the previous chapter we have shown that the conductivity of Ag₂S is strongly dependent on the stoichiometry. Hence, to study the conductance and switching properties of Ag₂S thin films we need a sample preparation technique, which is reproducible and that results in thin films with the desired stoichiometry.

Thin films of α -Ag₂S have been prepared by different methods in several research groups, which include the use of silver sulfide pellets for the very first investigations on Ag₂S [35, 42], to newer methods as chemical vapor deposition (CVD) [43], chemical bath deposition (CBD) [44, 45] and thermal evaporation [32, 46]. For the growth of our Ag₂S devices we investigated two different methods. One is the sulfurization of a Ag thin film in vacuum, and the second is Ag sputtering in a Ar/H₂S atmosphere.

Silver sulfurization is the conversion of a Ag thin film to Ag₂S by reaction with sulfur vapor,

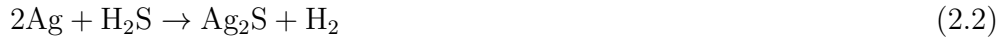


It is a relatively simple method and it can be performed in UHV [46], HV [47, 48] and even at atmospheric pressure [49], and at temperatures ranging from room temperature up to approximately 700 K, depending on the pressure and setup. Because of the single oxidation state of Ag, the sulfurization of a Ag film usually results in a single phase material (for example acanthite, the room temperature phase). Sulfurization of other transition metals, can result in multiple phases due to the several possible oxidation states. This is the case, for example, of copper sulfide. Copper sulfide has at least five phases at room temperature, defined by various stoichiometries and valence states, and therefore several phases can coexist in a single sulfurized Cu film [50, 51].

In the first section of this chapter, the specific sulfurization parameters used to grow our samples and the subsequent characterization of the thin films will be presented.

The second method is radiofrequency (RF) sputter deposition. The RF sputter deposition method is a slightly more complex technique. It consist of a vacuum

chamber, with a Ag target and a Si substrate mounted on a sample holder in front of the target. An Ar plasma is ignited between the target and the grounded sample holder. The Ar⁺-ions knock Ag atoms from the target, which deposit on the substrate, forming a Ag thin film. In addition to this, for the deposition of Ag₂S, we introduce H₂S into the chamber, which then reacts with Ag forming Ag₂S,



In this process, also called reactive sputtering, the partial pressure of the reactive gas in the chamber is a very important parameter to achieve the correct sample stoichiometry. RF sputter deposition is a widely used deposition method for industrial applications. It also allows deposition of metals and insulating materials, therefore it is a very appropriate method for the growth of chalcogenide thin films as demonstrated in [52, 53].

In the second section of this chapter, the specific sputter parameters used to grow our samples and the subsequent characterization will be presented.

2.2 Sulfurization of Silver Thin Films

The Ag₂S devices are grown on clean Si (100) substrates with a native oxide layer. The fabrication steps are presented in Fig.2.1. First, a layer of Pt (100nm thickness and 10x10 mm² surface area) is sputtered onto the substrate, followed by a layer of Ag (200nm thickness and 5x5 mm² surface area) which is sputtered using a shadow mask. After sputtering follows the synthesis of Ag₂S by sulfurization of the Ag film. Sulfur powder (reagent grade powder purified by sublimation) is loaded into a quartz tube (18mm internal diameter) and the sample is held at 10 cm vertical distance facing the sulfur powder. Once the sulfur and the sample are loaded, the tube is evacuated to a pressure of 1 x 10⁻⁶ mbar. The temperature in the tube is then increased to 523 K (± 3K) using a vertical furnace with a programmable temperature control. The tube is kept under static vacuum to create a sulfur atmosphere, while the temperature remains constant at 523 K (± 3K) for one hour. After one hour, the tube is evacuated but kept at 523 K (± 3K) to anneal the samples during one more hour. Finally, the sample is slowly cooled down to room temperature at a rate of 1 K/min.

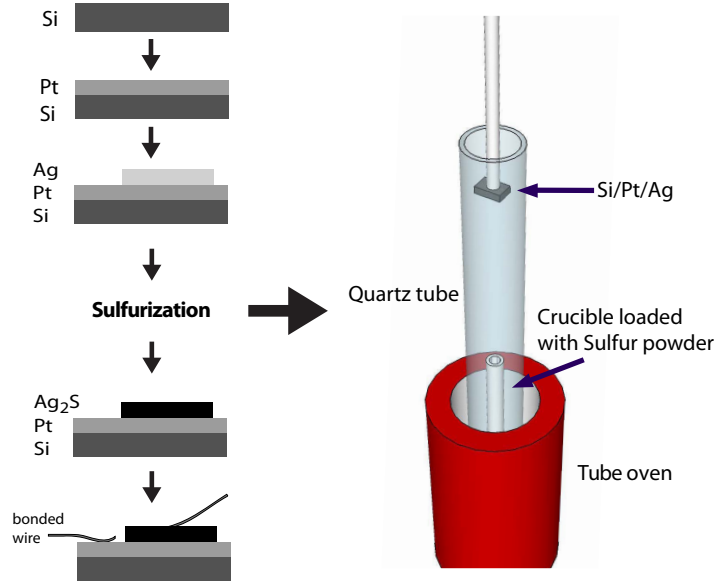


Figure 2.1: Schematic diagram of the fabrication steps of the Ag₂S devices and drawing of the oven set up used to sulfurize the Ag thin films.

Sulfurization starts with a direct reaction of Ag atoms on or near the surface of the film, with the S vapor forming a Ag₂S layer. During the sulfurization, the sample is held at a temperature above the phase transition temperature of 451 K, therefore, the initially formed Ag₂S is in the β -phase. This phase is characterized by a very large Ag ion mobility. This large mobility together with the high temperature, allows a continuous reaction of the sulfur vapor with the diffusing Ag atoms on the growing surface. When cooling down, a phase transition should occur from β to α -Ag₂S. We cooled down the samples after annealing at a slow rate (1K/min) to avoid frozen-in argentite β -Ag₂S crystals within the acanthite α -Ag₂S films [45, 46].

Powder X-ray diffraction (XRD) patterns were taken at room temperature using a Phillips X'Pert Pro diffractometer. The spectra indicate the formation of acanthite Ag₂S (Fig.2.2a). The highest intensity peaks of the spectra correspond to the (012) and (013) peaks of acanthite Ag₂S. In addition, the (-112), (-103), (103) and (014) peaks of α -Ag₂S are also present in the spectra.

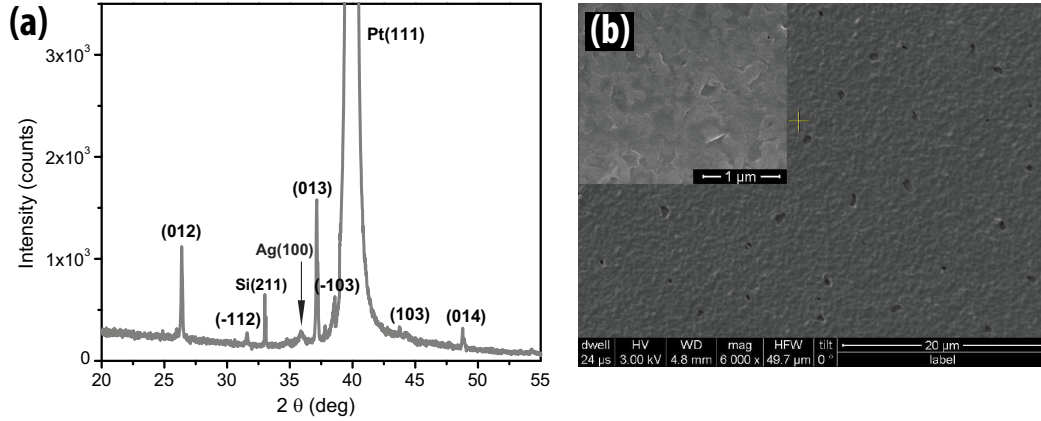


Figure 2.2: a) XRD spectra of the Ag_2S thin films deposited on top of a Pt layer. The observed peaks in the spectra correspond to Ag_2S . Additional peaks indicated in the spectra as Si(211), Ag(100) and Pt(111) correspond to the Si substrate, the Pt electrode at the bottom of the film and the Ag inclusions in the film. Rutherford backscattering spectroscopy (RBS) data of the Ag_2S devices confirmed that the observed Ag peak is not a remaining Ag layer between the Pt and the Ag_2S . b) SEM top view of the surface morphology for a typical Ag_2S sample scanned with an electron beam energy of 3kV. A fairly smooth surface is observed with holes at some locations, as more clearly seen in a close-up view of the surface morphology as presented in the inset.

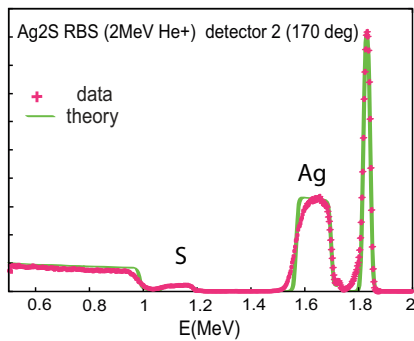


Figure 2.3: Rutherford backscattering spectroscopy (RBS) data of the Ag_2S devices. A comparison with the theoretical spectra of Ag_2S is used to indicate the formation of stoichiometric samples. The observed divergence from the theoretical data is due to the film roughness.

We expect from literature (JCPDS file 14-0072) that the strongest diffraction peaks are the (-103) and (-112). We find the strongest intensity at the (013) and (012) peaks. The difference in the intensity of the diffraction peaks can be explained by a preferential orientation that the crystal domains acquire during the growth process. In spite of the difference in intensity between the recorded spectra and the expected values, all peaks are found at the correct θ value. This

latter observation confirms that the material probed by XRD is indeed acanthite Ag₂S. Additional peaks are also observed in the spectra. The narrow peak at $\theta = 33.01^\circ$ corresponds to the (211) peak of crystalline Si (JCPDS file 14-0072) and is coming from the substrate. At $\theta = 35.9^\circ$ a broad peak is observed, indicating the presence of disordered metallic Ag (JCPDS file 87-0598). This may indicate small inclusions of the initial Ag film that did not react during sulfurization. Finally, a strong Pt peak is observed at $\theta = 39.9^\circ$, due to the exposed area of the Pt film on the sample. The stoichiometric ratio of Ag:S = 2:1 was confirmed by Rutherford Back Scattering (RBS). Figure 2.3 shows the spectrum obtained from one of our samples compared to the theoretical spectrum for stoichiometric Ag₂S. In addition to the Ag and S signals, in the measured sample we observed the signal from the Si substrate and a top Au thin layer.

The surface morphology of the as-grown films was examined by scanning electron microscopy (SEM) at low electron beam energies (3-5 kV). In Fig.2.2c we present the typical surface morphology of the Ag₂S films. In this image a fairly smooth surface is observed. The appearance of holes at some locations of the film is probably caused by the cooling down process, where a phase transition from β to α phase occurs. This phase transition corresponds to a volume contraction and an increased lattice disorder [54]. Apart from the phase transition, another cause could be a difference in the thermal expansion between the Ag₂S and the Pt bottom electrode, however, to our knowledge this has not been reported in literature.

At high electron beam energies, from 10 to 15 kV, the precipitation of Ag protrusions on the surface towards the electron beam is clearly observed. Figure 2.4a-h presents frames of a movie (in chronological order from a to h) recorded while imaging the Ag₂S surface. The white spots on the surface are the Ag protrusions that grow spontaneously as a result of the exposure to the electron beam. The zoomed in image (Fig.2.4d) shows the size of the Ag protrusions of approximately 100 nm diameter. The zoomed out images (Fig.2.4e-h) shows the modification caused on the exposed region of the film as well as the precipitation of more Ag filaments in the newly exposed area.

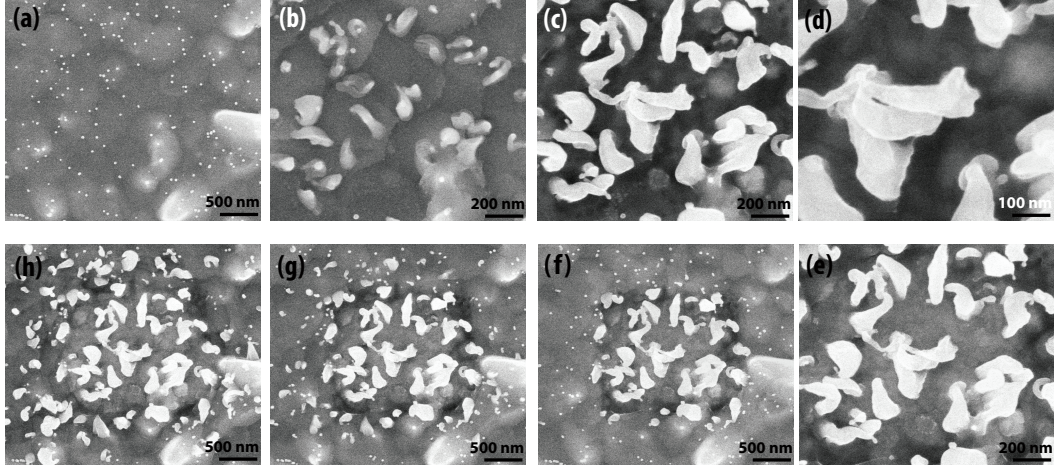


Figure 2.4: Precipitation of Ag protrusions at the surface of the Ag_2S film observed by scanning electron microscope (SEM). The figures from (a) to (h) are frames (in chronological order) of a movie recorded while zooming in and out on the surface.

2.2.1 Ag_2S Single Crystal Whiskers

An interesting effect observed when tuning the parameters for the sulfurization of Ag films, is the formation of Ag_2S single crystal whiskers that grow from the sample surface. These whiskers grow to sizes of several micrometers in length and approximately $1 \mu\text{m}$ wide, presenting well defined facets on the lateral surfaces. Figure 2.5 presents SEM images of several whiskers found on different sulfurized Ag films. The bottom left image of Fig.2.5 presents the growing of Ag protrusions on one whisker induced by the electron beam.

The formation of Ag_2S whiskers has been previously observed on Ag_2S samples prepared by sulfurization [55, 56], and its formation mechanism has been explained to be analogous to the Vapor-Liquid-Solid (VLS) mechanism [57]. The process consist of the formation of a Ag_2S droplet, which acts as the nucleation site for the whisker growth. Under a constant S vapor pressure, the Ag_2S whisker will then grow along the energetically favorable crystal orientation. According to the authors [55] the presence of a catalyst particle at the end of the whisker was not always observed, which was explained by the non-stability of the droplet at specific thermodynamic conditions. In our whiskers we did not observe the presence of a catalyst particle at the end of the whiskers.

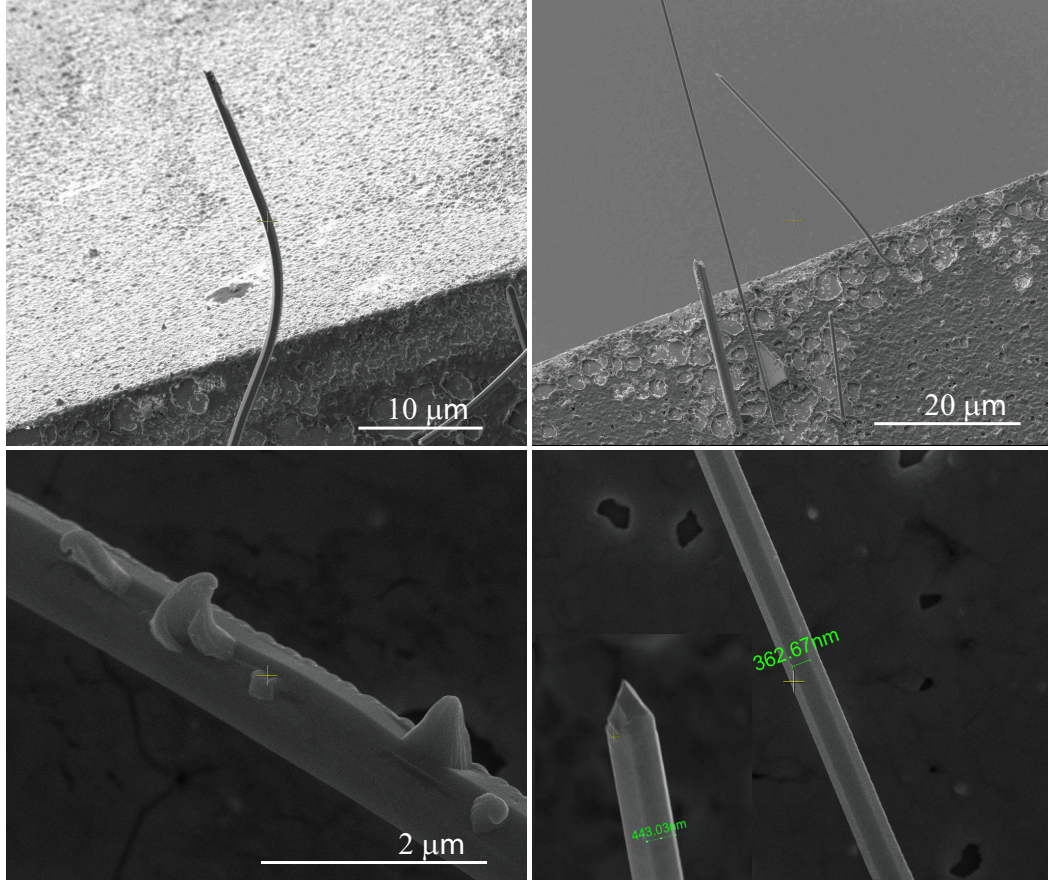


Figure 2.5: Scanning electron micrograph of several whiskers formed on sulfurized Ag₂S thin films. The bottom left picture shows Ag protrusions growing from the whisker activated by the electron beam.

With our Ag sulfurization method, the main parameter that differentiates from obtaining either a smooth sulfurized film, or a film with whiskers growing on the surface is the sulfurization time (the whiskers grow at sulfurization times longer than the typical 2 hours used for the films). A low S vapor pressure in the tube is another parameter that possibly influences the whisker growth, although this was not confirmed. We analyzed the composition of the whiskers by energy dispersive spectroscopy (EDS) and the result is presented in Fig.2.6a. The EDS spectra confirm that the whiskers are composed of only Ag and S atoms, and with an atomic percentage of 67.1% Ag and 32.9% S ($\pm 0.1\%$).

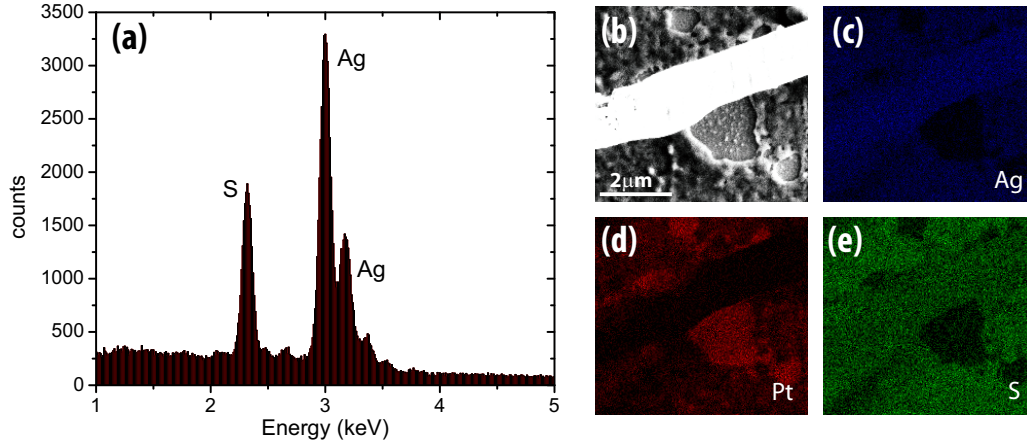


Figure 2.6: a) EDS spectrum acquired on the whisker presented in (b). The spectrum indicates Ag content of 67.1% and S content of 32.9% in atomic percentage. Elemental mapping showing the distribution of c) Ag and d) S content on the whisker and the sample surface. e) Pt content map indicating its presence only on the surface of the sample.

2.2.2 Summary

The characterization of the samples fabricated by Ag sulfurization, indicate that this is a reliable method to obtain acanthite (α -) Ag_2S films. This method presents the advantage that is simple and can be easily implemented in the fabrication of layered devices of the form $\text{Si}/\text{Pt}/\text{Ag}_2\text{S}$. On the other hand, we have learned that parameters as temperature, sulfurization time and cooling down rate strongly influence the formation of holes in the film or grow of whiskers. Another disadvantage is the controllability of the Ag_2S layer thickness and therefore the formation of a well defined $\text{Ag}/\text{Ag}_2\text{S}$ interface. This is important in the fabrication of devices with the layers $\text{Si}/\text{Ag}/\text{Ag}_2\text{S}$. The advantage of having a Ag bottom electrode instead of Pt is the fact that Ag fixes the chemical potential at the $\text{Ag}/\text{Ag}_2\text{S}$ interface, and therefore, the stoichiometry is also fixed at the maximum in equilibrium with Ag. The sulfurization method as we performed it, did not reproducibly allow the control of the Ag film thickness to be sulfurized, to keep one clean (no sulfurized) Ag bottom electrode. To achieve this, we used the second method that is reactive sputtering.

2.3 Reactive Sputtering of Ag₂S thin films

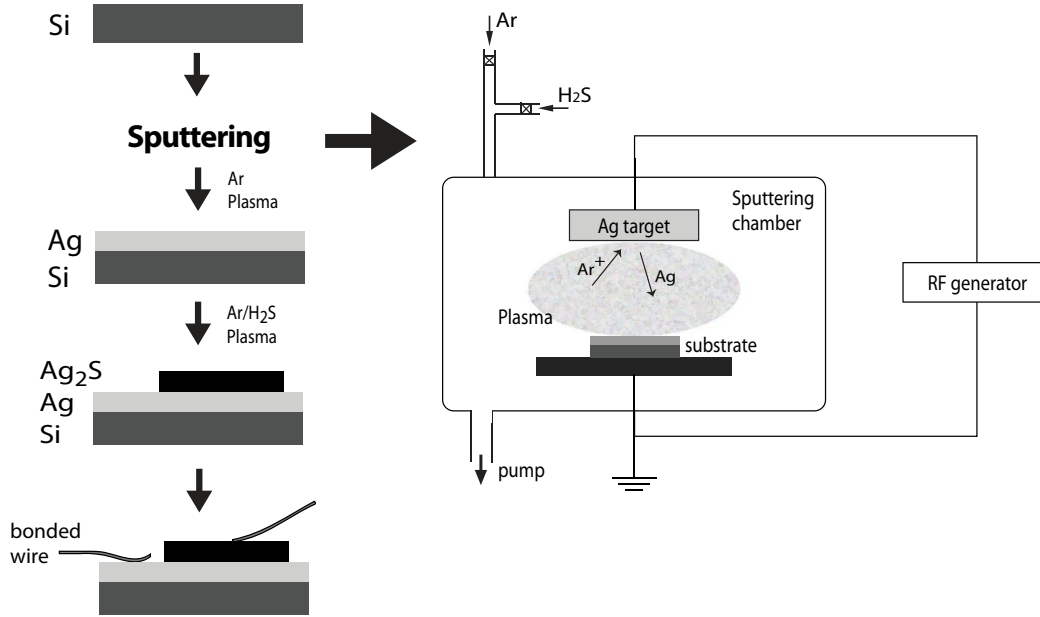


Figure 2.7: Schematic diagram of the fabrication steps of the Ag₂S devices and drawing of the sputtering system used to grow the samples.

For the fabrication of Ag₂S devices by reactive ion sputtering we used a specialized Leybold Z-400 RF diode sputtering system equipped with one silver target and 2-channel gas blending for Ar and H₂S. The fabrication steps are presented in Fig.2.7. A layer of Ag (100nm thickness and 10 x 10 mm² surface area) is sputtered onto a clean Si(100) substrate covered with a native oxide layer. On top of the Ag layer, the Ag₂S layer (200nm thickness and 5 x 5 mm² surface area) is grown by sputtering of Ag in a Ar/H₂S plasma, with the use of a shadow mask. For the preparation of stoichiometric Ag₂S by RF-sputtering, the most important parameter is the partial pressure of H₂S in the sputtering atmosphere. To estimate the partial pressure of H₂S in the sputtering chamber, we measure the total pressure ($P_{\text{total}} = P_{\text{H}_2\text{S}} + P_{\text{Ar}}$) with a Compact Capacitance Gauge (CMR 264, Pfeiffer Vacuum). First the Ar partial pressure is set to establish the sputtering discharge (pre-sputtering), and only then, H₂S is introduced in the chamber. To achieve a stoichiometric composition, the partial pressure of H₂S used is $\approx 6 \times 10^{-4}$ mbar. Once the plasma, pressure and gas flow are stable, the sputtering

deposition is performed. The deposition process is all at room temperature and no post-deposition treatment was carried out on the samples.

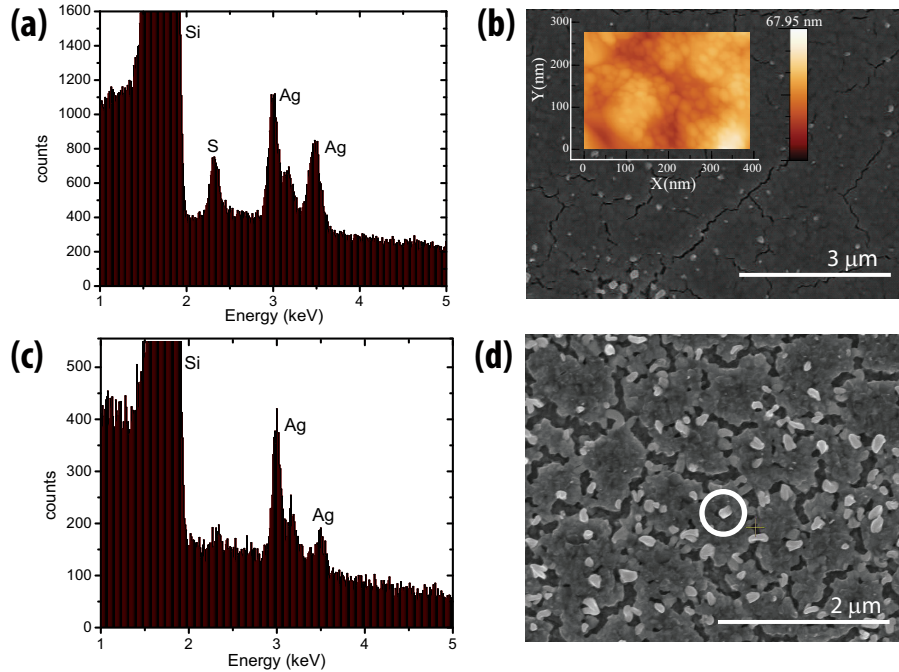


Figure 2.8: a) EDS spectrum of a sputtered Ag_2S film deposited on a Si substrate on top of a previously sputtered Ag layer. The observed peaks indicate the Ag and S content on the film, as well as a Si peak of the substrate. b) Surface morphology of a typical sputtered Ag_2S film examined by SEM and AFM (inset). The cracks on the surface are caused by the exposure of the film to the electron beam, and therefore the formation of Ag protrusions (white spots on the surface). These cracks become larger at longer exposure times. c) EDS spectrum of one of the Ag filaments growing on the surface of the film (the encircled filament in the SEM scan presented in (d)). The observed peaks indicate the presence of Ag but negligible S content on the protrusion.

The composition of the samples was analyzed by x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS). The XRD spectra did not show as clear Ag_2S peaks as for the sulfurized samples, suggesting the formation of an amorphous or nanocrystalline film. The chemical composition was therefore checked by EDS. We used a FEI XL30 SEM equipped with an EDS system from the FOM Amsterdam nanocenter facilities. The spectra (Fig.2.8a) were taken at 10 kV electron beam energy and show the presence of the elements Si, Ag and S.

The dominant Ag peaks correspond to the characteristic x-ray lines of the L series 2.985, 3.151 and 3.511 keV. The S peak corresponds to the characteristic x-ray line 2.308 keV of the K Series. Discarding the Si content, the spectra indicate atomic percentages of 66.7% Ag and 33.3% S ($\pm 0.1\%$). The presence of the Ag bottom electrode was confirmed by testing the resistance of the bottom layer and by XRD. The formation of semiconducting Ag₂S and the sample stoichiometry was confirmed with electrical transport measurements. This will be presented in Chapters 4 and 5.

The surface morphology of the sputtered samples was examined by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Figure 2.8b shows a SEM micrograph of the surface morphology of a sputtered Ag₂S film. The inset shows an AFM topography image of the surface. We observe a rough surface with grain sizes of approximately 20 to 40 nm diameter. Figure 2.8d shows a closer view of the sample surface with Ag protrusions activated by the electron beam. An EDS spectrum was taken at the Ag protrusion (white circle in the figure) showing only the elemental Ag peaks (Figure 2.8c) and a vanishing of the S peak. No Ag₂S whiskers were formed on samples prepared using the sputtering method.

2.3.1 Summary

Sputtering deposition allows the fabrication of devices with Ag or Pt bottom electrodes. This method presents the advantage of Ag and Ag₂S layer thickness deposition control and a continuous film without holes, in contrast to the sulfurization method. The absence of whiskers is also an advantage of this technique. Growth of the films at room temperature leads to the formation of amorphous or nanocrystalline Ag₂S films.

2.4 Fabrication of in-plane electrodes and Ag₂S deposition issues

In section 2.2 and 2.3 it was shown that either sulfurization of a Ag thin film, or reactive sputtering, are appropriate methods for the fabrication of so called out-of-plane devices, layered devices of the form Si/X/ α -Ag₂S/Pt(nano- top contact), with X = Pt or Ag. For these devices the electrical measurements are performed

perpendicularly across the Ag_2S layer. A large part of our investigations was performed with these devices using different top electrodes, as will be presented in Chapters 3, 4, 5 and 6. Although it is important to study the electrical switching properties, for these devices the direct visualization of Ag nanowire formation in Ag_2S is not possible. To achieve this we fabricated so called in-plane devices, where the electrical measurements are performed parallel to the surface of the Ag_2S thin films. We combined electron beam lithography techniques to pattern the electrode structure, conventional deposition techniques to deposit the Pt electrodes, and the sulfurization or the sputtering method to deposit the Ag_2S layer. The results and challenges found in the fabrication of these devices are presented below.

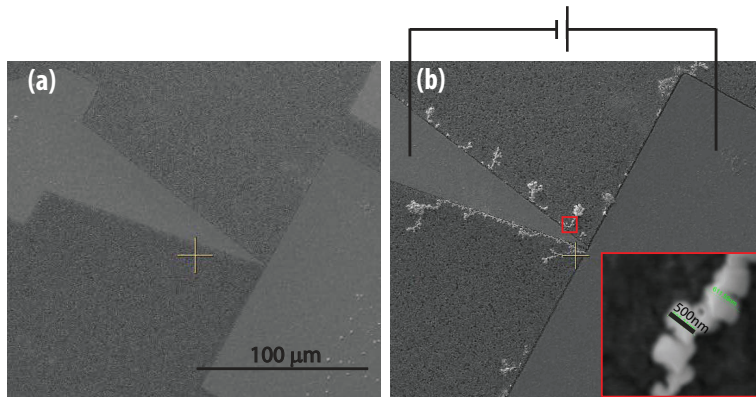


Figure 2.9: Scanning electron micrograph of a two terminal in-plane device. The gap between the electrodes is approximately $1\mu\text{m}$. a) Pt electrodes with the Ag_2S layer deposited on top before the activation of the device. b) When a voltage difference is applied between the electrodes, Ag filaments formed at the regions close to the negatively biased pointed electrode.

Using e-beam lithography (EBL), Pt electrodes were patterned on a Si wafer with a native oxide layer. Each pair of electrodes formed a gap of few micrometers or few tens of nanometers. Ag_2S was deposited on top of the electrode structure centered at the gap between the electrodes. The Ag_2S layer therefore contacts the two electrodes forming a two terminal device of the form Pt/ Ag_2S /Pt. The first in-plane devices were fabricated with the geometry presented in Fig.2.9. The Pt electrodes are separated by a gap of approximately $1\mu\text{m}$. The Ag_2S layer on top of the electrodes was deposited by reactive sputtering as described in section

1.3. In-situ electrical measurements performed in the SEM showed that, when a voltage was applied between the electrodes, the growth of small Ag filaments was induced, as presented in Fig.2.9b.

Aiming for the formation of a Ag bridge between the electrodes with atomic scale sizes, we proceeded with the fabrication of much smaller devices, i.e., devices with nanogaps between the electrodes. The nanoscale devices were fabricated partly in the Nanolab Groningen facilities (fabrication of the Pt electrodes), and in our laboratory in Leiden (the deposition of the Ag₂S layer). At these dimensions the Ag₂S deposition methods, both sputtering and sulfurization, did not result in good Ag₂S films. Figure 2.10b-c present the result of the Ag₂S deposition by sulfurization of a Ag film on the nanoscale electrodes presented in Fig.2.10a. The SEM images indicate that the Ag shrinks into clusters of Ag or Ag₂S. It is important to mention that for the sulfurization of the Ag nanosquare areas, the sulfurization parameters were adjusted to a sulfurization temperature of 420 K and a sulfurization time of only 30 min without further annealing. Figure 2.11b-d presents the result of the Ag₂S deposition by reactive sputtering on the electrodes given in Fig.2.11a. The SEM images show the formation of non-continuous films and the disappearance of a previously deposited Ag electrode. The sputtering parameters were the same as those presented in Section 2.3.

A possible explanation as to why the deposition of Ag₂S in such small areas was not successful, may be the lack of an adhesion layer on the Si (for example Cr or Ti) before the evaporation of Ag or sputtering of Ag₂S. Another explanation could be that the deposited film thickness was not enough to form a continuous layer. The last problem is related to the compromise between the resist layer thickness and the thickness of the deposited layer to achieve a good lift-off process. Fine-tuning of the sputtering parameters (the partial pressure of H₂S on the chamber and slower deposition rate) or fine tuning of the sulfurization parameters (much lower temperatures and shorter sulfurization times) will be required for the successful fabrication of lithographically patterned nano-Ag₂S. Direct evaporation of Ag₂S powder could be a good alternative to the presented methods.

Because of research priorities and estimated time needed for the optimization of EBL fabrication parameters, we did not proceed with this type of samples.

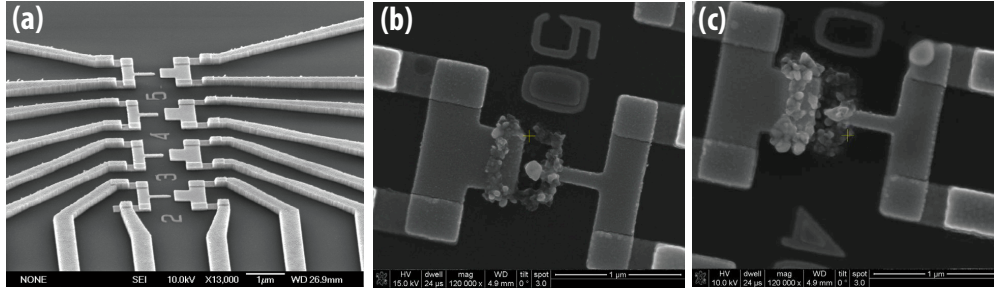


Figure 2.10: a) Scanning electron micrograph of two terminal devices, each pair of electrodes separated by 20, 30, 40 and 50 nm gaps. b) and c) Result after deposition of Ag and sulfurization at 420 K.

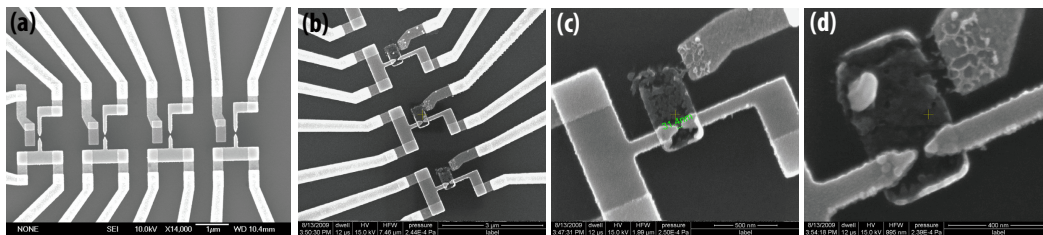


Figure 2.11: a) Scanning electron micrograph of three terminal devices, formed by Pt electrodes separated by nanogaps of 30 nm and a Ag third electrode. b, c, d) Result after reactive sputtered deposition of Ag_2S in the nanoscale area between the electrodes.

2.5 Conclusions

Two fabrication methods were presented in this chapter. Both sulfurization and reactive sputtering are suitable for the growth of semiconducting Ag_2S thin films. The silver sulfide samples prepared by sulfurization of a Ag thin film are polycrystalline. A side effect of the high temperature and sulfur vapor pressure used in this method, is the formation of micrometer long whiskers. Silver sulfide samples prepared by reactive sputtering are possibly amorphous or nanocrystalline (no clear X-ray peaks observed), the films are continuous and the samples do not present evidence for the formation of whiskers. For a good control of the growth parameters and a well defined Ag/ Ag_2S interface, the reactive sputtering method is the most suitable fabrication process. Both types of Ag_2S fabrication processes need to be further tuned for application in EBL fabricated devices.

2. Ag₂S: FABRICATION AND CHARACTERIZATION TECHNIQUES
