Chalcogenide Letters Vol. 13, No. 5, May 2016, p. 201 - 206

ABSORBANCE AND CURRENT-VOLTAGE HYSTERESIS CURVE OF SILVER SULFIDE THIN FILMS SYNTHETIZED BY SOLID-VAPOR REACTIONS

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Silver sulfide thin films (Ag_2S) with thickness ranging from 90 to 290 nm were synthesizedusing a low temperature (110°C) solid-vapor reaction by sulfurizing(3h) sputtered silver on glass substrates.Samples were characterized by X-Ray diffraction, Field Emission Gun Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy. In addition, optical and electrical properties were investigated using an Ultraviolet-Visible Spectrophotometer and a Physical Properties Measurement System.Results showsband gaps in the range of 1.7 to 2.6 eV that are dependent on the film thickness. Electrical propertiesexhibit a hysteresis I-V curve that is characteristic of memory devices and can be attributed to the Ag^+ ions migration inside the Ag_2S film forming conducting filaments.

(Received March 18, 2016; Accepted May 5, 2016)

Keywords: Silver sulfide;solid vapor reaction; thin films; absorbance; I-V hysteresis curve.

1. Introduction

Chalcogenides semiconductors thin films such as selenides, tellurium, and sulfides have important optical and electrical properties with relevant applications in numerous fields of science research and applied technology[1]. Silver sulfide is an ionic and electronic conductor, which is found in three phases: α-Ag_2S, known as Acanthite that has a monoclinic structure and is stable at room temperature, β-Ag_2S phase, recognized as Argentite which has a BCC structure and is stable at a temperature range of 178 to 600°C. Lastly, the γ-Ag_2S has a FCC structure and is stable at 600 to 825°C[2]. Several researchers are paying close attention to silver sulfide (Ag_2S)because this chalcogenide has been used in various optical and electronical devices showing promissory results, such as photoconducting cells, infra-red detectors, solar selective coatings, photoconductor, photovoltaic cells, memristors and nanoswitches[3-8].K.Terabeet al. reported in 2005 the possible use of α-Ag_2S on atomic switches and describe the quantum point mechanism employed by these devices[7]. They found that nano-protrusions of silver can be created on a silver sulfide surfaceand are related to a solid electrochemical reaction controlled by the polarity of the voltage applied[7]. T. Ohno et al. demonstrated the Ag_2S potential application in short-term memoriesunder applications of low range of voltage pulses[9].Dias [8] concluded that Ag2S has potential properties for memristivenano-ionic devices and resistive switching for the fabrication of artificial neural networks.

Several research groups have reported different silver sulfide thin films synthesis methodsincludingChemical Vapor Deposition, Ion Beam Deposition, Solid-Gas Reactions, Electrodepositionand Chemical Bath[1,3,8,10-12].However, some of these methods use high temperature during the synthesis process(above400°C) [1] or additional annealing processesare required[1]. The use of high temperatures does not allow the synthesis of the filmson flexiblesubstrates[3,4,13].

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The main purpose of this work is to synthesize silver sulfide thin filmsusinglow temperature solid-vapor reactions and understand the films thicknessesand morphologieseffects on their properties for application on optical and electronical devices.The proposed synthesis technique has several advantages such as simplicity, low cost, low processing temperature and low by-products formation [14-16].

2. Experimental details

Silver sulfide was synthesized by solid-vapor reactions using glass substrates of 20 x 25 x 0.5 mm. Sputtering deposition technique was used to obtain thin films of silver on glass substrates.A 99.9 % silver target from Ted Pella Inc. (P/N 91118) was used. The deposition time was varied from2 to 5 min at 0.075 Torr, room temperatureand 20 mA in an argon atmosphere.After the silver deposition process, the silver coated substrates were sulfurized by solid-vapor reactions. The samples were placed during 3 h into a beaker with 30 mL of deionized water and 3 g of sulfur at 110°C and 1atm[16]. The resulting films were analyzed, using Field Emission Gun Scanning Electron Microscopy (Jeol JSM-7000F) and Grazing incidence diffraction (GIXD) (RigakuUltima III X-ray diffractometer). Transmittancespectra of the films were obtained with a UV-Vis spectrophotometer (Perkin-Elmer Lambda 24 UV-Vis spectrophotometer).The filmsthicknesses were measured by image analysis. The electrical properties were obtained by a Physical Properties Measurement System (Versa Lab Free Quantum Design) using silver contacts.

3. Results and discussion

The resulting thin films wereidentified by GIXD as α-Ag_2S (acanthite phase) referencing the PDF card 01-089-3840 and calculated from ICSD using POWD-12^{++} of the PANanalyticalX'pert PDF2 2003 database (see Figure 1). Most intense peaks appear at 2θ values of 28.9, 31.5 and 33.6, which are the most intense peaksreported for α-Ag_2S[15].

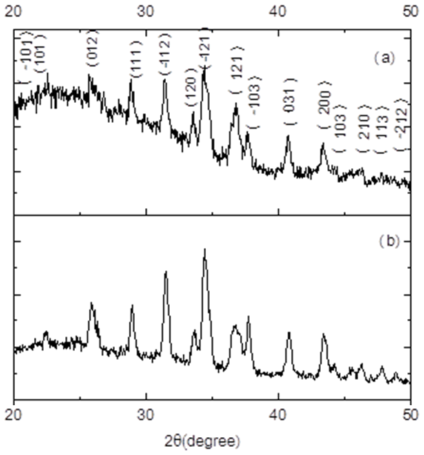

Fig. 1. a) and b) GIXD pattern of 2 and 5 min deposition time samples. Sulfuring time was 3h.

Figure 2 shows the effect of the deposition time on the films thickness. It is seen that after sulfidation the thickness tends to increase due to the solid vapor reaction occurring between the silver and the reactive sulfur in the environment. This reaction produceshigh surface area structures of Ag_2S due to the layered growing mechanism reported in our previous work. Excess of sulfur in the atmosphere can form an unstable compound Ag_2S_2. Then, silverionsdiffusethroughthesilversulfidelayertoreactwiththeunstablecompoundformed at thesurfaceand withthesulfur in theatmospheretoform more Ag_2S [14,15]. Proposedreactions are as follows[14,15]:

$$2Ag + S^{2-} = Ag_2S + 2e^{-} \quad (1)$$

$$Ag_2S + S^{2-} = Ag_2S_2 + 2e^{-} \quad (2)$$

$$2Ag + Ag_2S_2 + 2e^{-} = 2Ag_2S \quad (3)$$

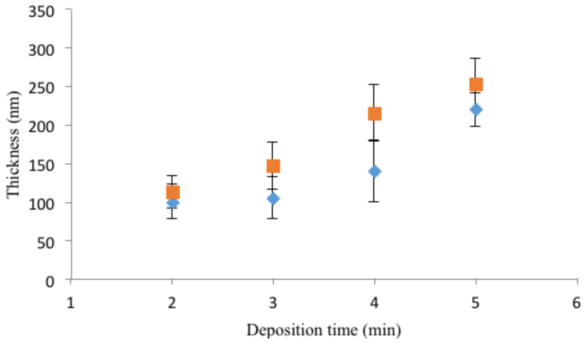

Fig 2.Films thicknesses before (blue) and after (orange) sulfidation.

The thin films morphology at different silver deposition times after 3 h of sulfidation is shown in Figure 3. Films structure homogeneity increases as silver deposition time increases and structure size decreases. This is because the larger amounts of silver in the thicker films favor diffusion and nucleation whereas in the thinner films, after all silver reacts, the structure growth is favored during the sulfidation time.

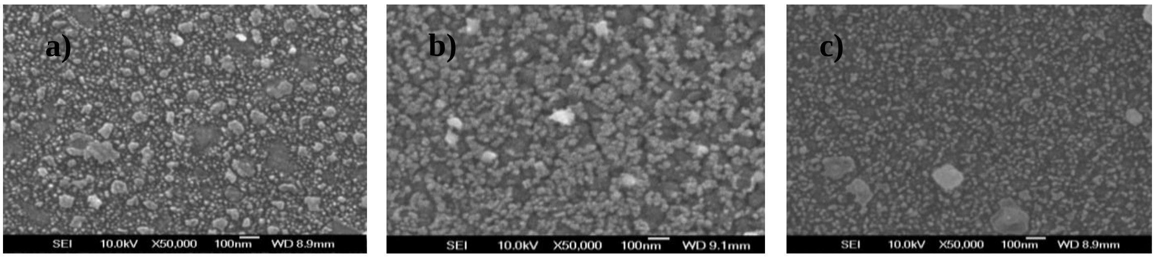

Fig. 3.SEM morphology of the thin films. a) 3min, b) 4 min, and c)5 min deposition time samples. Sulfuring process time was 3h.

Figure 4shows thethickness effect of Ag_2S thin films on the optical properties.The absorbance increases significatively asthickness increases. Moreover, the smaller structures in the samples with the larger deposition time increase the light scattering reducing the films transmittance. The direct band gap values at different deposition time were calculated from the $(\alpha h\nu)^2$vs hv graphs as shown in Figure 5. They varied from 1.7 to 2.6 eV according the films thicknessess and these values are in agreement with the wide range reported for Ag_2S thin films [17-20]. As expected, the thickest films show the lowest values. The effect of differences in thickness is larger than the effect of differences in the structure´s size. The wide range of bandgap variations allowsapplying these films in several fields such as solar radiation absorberand optoelectronic devices[13, 20-24].

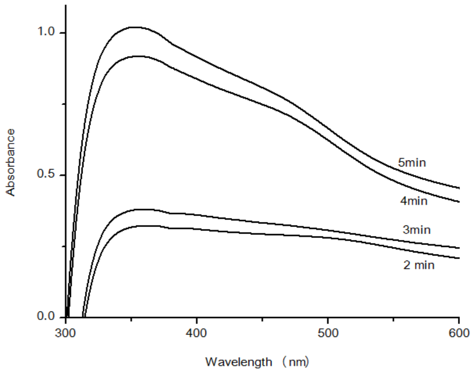

Fig. 4.Absorbance of the thin films at different deposition time samples. Sulfuring process time was 3h.

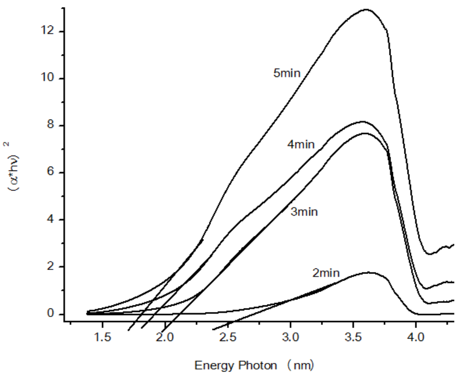

Fig. 5.Direct band gap values of 2 to 5min of deposition samples. Sulfuring process time was 3h.

Figure 6shows the I-V curves for the synthetized films where hysteresis loops are observed. These loops are reported as typical signature of memory devices[25]. Ag^+ ion migration (from the electrical contacts used for measurement) and filaments formation occur causing the hysteresis loop. Recently, several authors demonstrated that Ag_2S can be used for memristivenano-ionic devices and resistive switching. In these devices, the ion transport is fundamental as reported by[5,6, 26,27]in Ag/Ag_2S systems.For example, Morales et al. in their swithicingresistive study of Ag_2S/Ag systems reported Ag^+ ions migration at the Ag_2S film surface and inside the film forming filament[27]. Conducting filaments act as a circuit switch between electrodes. Filaments initial growth is due to the applied electrical field and the applied voltage aids into filaments directionalityduring their nucleation and growth. Dias et al. also confirmed filament formation inside the Ag rich Ag_2S thin films showing I-V curves with hysteresis loops for memresistivedevices[8]. They show in their films, mainly eight shaped I-V curve. In the case of this work, the hysteresis loops do not present eight shapes, instead a coercive voltage is observed.The thickest films with the smalleststructure´s size are the ones that show the highest coercive voltage and the lowest current.Thisbehavior could be related to the larger amounts of structural defects present in these films. These defects are due to the layered growing mechanism explained before and they could reducethe current flow and allowthe voltagestorage.

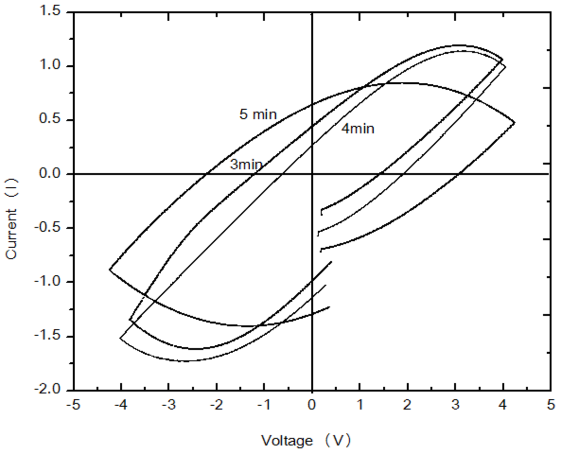

Fig. 6. I-V hysteresis curves at room temperature of 3 to 5 min of deposition time samples. Sulfuring time was 3h.

4. Conclusions

Silver sulfide (acanthite-Ag_2S) thin films in the range of 90 to 290 nm were synthtized by simple solid-vapor reactions at 110^oC and 1 atm. Films thickness variations allow absorbances increase from 40 to 90% at wavelengths from 300 to 600 nm. The optical energy band gaps values varied from 1.7 to 2.6 eV. I-V curves of the films showed hysteresis loops characteristic of memory devices. According to the measured optical and electrical properties, these films could potentiallybeused inoptical and electronic devices. The low temperature used in this synthesis method allows these films to be applied on flexible substrates.

Aknowledgments

Authors thank SEP-CONACYT for the financial support grant No. 168039 and CONACYT scholarship No. 559574.

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