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CHARACTERIZATION OF Cu_xS THIN FILMS OBTAINED BY CBD TECHNIQUE AT DIFFERENTS ANNEALING TEMPERATURES

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Copper sulfide thin films were grown on glass substrates at 40 ºC by the chemical bath deposition technique and post treated in air, nitrogen and vacuum atmospheres during 40 minutes at different temperatures. The [Cu]/[S] concentrations ratios were varied in order to change the thiourea concentration in the range of 1 to 3.0 in steps of 0.5. The thin films obtained were annealed varying the temperature of treatment from 75 to 300 °C. Three copper sulfide phases were observed, which depend on the annealing atmosphere and temperature. A conductivity of 7.26×10^{-4} Ω-cm is achieved at 200 ºC in a vacuum atmosphere. The band gap varied from 1.8 to 2.4 eV. The transmittances of the films were in the 50 to 90 % range. X-ray and SEM analysis showed that all the films were nanocrsytalline.

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1. Introduction

Nowadays, nontoxic and abundant materials in the earth´s crust, such as the transition metal chalcogenides, are an important point of study for the development of technological materials. The research on transition metal has been on sulfides, tellurides and oxides. The research on chalcogenides has been rapidly expanding due to their excellent physical and chemical properties. Their potential has been recognized for optical sensors, microelectronic devices, laser sources catalysts, microwave shielding coatings, electroconductive electrodes, sensors for low and room temperatures, photothermal conversion, solar control coatings and solar energy conversion [1-4]. Its variable stoichiometry that gives variation in valence states of the cupper, morphology results in crystalline to amorphous, optical and electrical unique properties [5-7]. The copper sulfur system (Cu_xS) has five stable phases that exist in nature: chalcocite (Cu_2S), djulerite ($Cu_{1.97}S$), digenite ($Cu_{1.8}S$), anilite ($Cu_{1.75}S$) ($Cu_{1.4}S$) and yarrowite ($Cu_{1.12}S$) this are referred to as blaubleibender covellite [8-10]. The structure of chalcocite and djulerite is hexagonal with alternate layers of copper and sulfur ions. The covellite contains 6 formula units in the unit cell with four copper ions tetrahedrally cordinated and two triangular coordinates with a hexagonal crystal structure with space group $P6_3/mmc$ (D^4_{6h}) [11, 12].

In the present study, analysis of the electrical, morphological and structural properties under different conditions such as [Cu]/[S] ratios, annealing temperatures and atmospheres were studied to understand the role of these conditions in the structure-properties relationship of the Cu_XS thin films obtained by the Chemical Bath deposition Technique. This study demonstrates the enhancement of the electro-structural performance of the nano-films due to a controlled annealing.

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2. Experimental procedure

The CuS thin films were grown on Corning glass slides by the CBD technique at 40 ± 1 ºC with a deposition time of 60 min. The glass slides were immersed vertically in an aqueous solution containing copper sulfate ($CuSO_4{\cdot}5H_2O$), sodium acetate (NaCOOH), Triethanolamine $(HOCH_2CH_2)_3N$, and thiourea (CH_4N_2S). The [Cu]/[S] ratios studied were 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0. Highly pure water (~18 MΩ) was used for the solution. The temperature was controlled in a hot plate equipped with magnetic stirring. Copper sulfate and thiourea were the sources of Cu^{2+} and S^{2-}, respectively. After the growth, the thin films were rinsed in highly pure water by ultrasonic cleaning for 10 min., and immediately followed by a thermal annealing process in an air, nitrogen and vacuum in a horizontal tubular furnace equipped with a quartz tube in the temperature range of 75-300 ºC. The samples were introduced into the quartz tube starting at room temperature with a ramp of 15 ºC/min.; the different annealing temperatures were kept constant for 50 minutes for all samples, and cooling slowly into the respectively atmosphere. Film thickness was measured in a profilometer (Sloan Dektak II) after removing a portion of the film with concentrated HCl. The dark resistivity was measured by the conventional four aligned probe method using a Loresta-6P, model MCP-T600. The ultraviolet-visible spectra were obtained in a Perkin-Elmer Lambda-2 spectrophotometer, in the 250–1100 nm wavelength range, using a glass substrate as reference. The SEM and EDS analysis were done with a JEOL Equipment.

3. Results and discusion

The Cu_xS thin films obtained by the chemical bath deposition (CBD) technique presented segregation after two to three weeks. In order to increase the stability of the films, an annealing treatment was carried out immediately after the deposition stage. The films were annealed in an air, nitrogen or vacuum atmosphere, all the films were then stable after 13 months, and highly adherent, dense and uniform.

The thin Cu_xS films were annealed as follows, in air ratios of [Cu]/[S] = 0.5, 1, 1.5, 2, 2.5 and 3 were studied ([Cu]/[S] =R). In nitrogen a vacuum atmospheres the only ratios probed were R= 0.5 and 1.0 because those had shown the best results. The annealing temperatures were 75, 100, 150, 200 and 250 °C. The Figure 1 a) shows air annealing transmittance values of all the concentrations and temperatures. The inset show the transmittance spectrum of ratios 0.5 and 1.0 at the annealing temperatures of 100 and 150 °C. The transmission values varied from 65 to 90 %. Figure 1 b), shown the transmittance of the concentrations (R=0.5 and 1.0) as a function of nitrogen annealing temperature (100, 150, 200 and 300 °C). In the inset we can observe the transmittance spectrum of Cu_xS thin films with R=0.5. The transmission values varying from 65 up to 90 percent, the transmission increases with the increase of the annealing temperature. In Figure 1 c) shown the transmittance of the concentrations (R=0.5 and 1.0) as a function of the vacuum annealed temperature (100, 150, 200 and 300 °C). The inset shows the transmittance spectrum of Cu_xS thin films with ratio of 0.5. The transmission decreases as a function of temperature increase (100-200 °C) after 200 °C the transmission begin to increase up to 72 %. The transmittance values varied from 50 to 72 % in an annealed vacuum atmosphere.

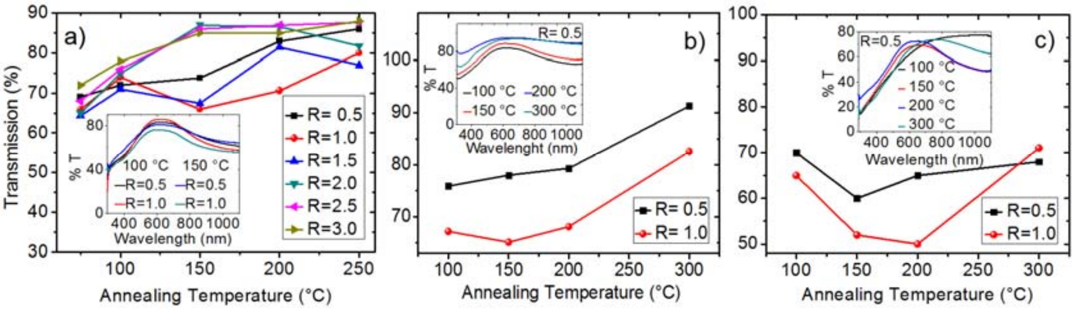

Fig. 1 Transmission of the Cu_xS thin films for several [Cu]/[S] ratios and annealing temperatures, a) air, b) nitrogen and c) vacuum atmosphere respectively

Fig.e 2 a) shown the variation of the band gap as a function of the [Cu]/[S] ratio and annealed temperature in an air atmosphere. The band gap varied from 1.8 up to 2.55 eV. In general the band gap decrease lightly from 75 to 150 °C annealed temperature, at 200 °C the gap began to increase. An analogous result has been obtained for Cu_2S thin films grown by different techniques [13-18, 24]. In Figure 2 b), we could observe the variation of the band gap as a function of R= 0.5 and 1.0 ratios and the annealed temperature in a nitrogen atmosphere. The band gap varied from 2.27 to 2.38 eV. The band gap increased from 100 to 200 °C annealed temperature, at 300 °C the gap decreased. Figure 2 c) shows the variation of the band gap as a function of R= 0.5 and 1.0 ratios and annealed temperature in a vacuum atmosphere. The band gap varied from 1.8 up to 2.36 eV. The band gap increased as the annealing temperature increased.

The increase of the band gap could be due to the formation of a mixture of phases of the copper sulfide as Cu_2S (Chalcocite), $Cu_{1.97}S$ (djulerite) and $Cu_{1.8}S$ (digenite). At high temperatures the increase of the band gaps may also be due to the loss of the sulfur and the formation of oxides.

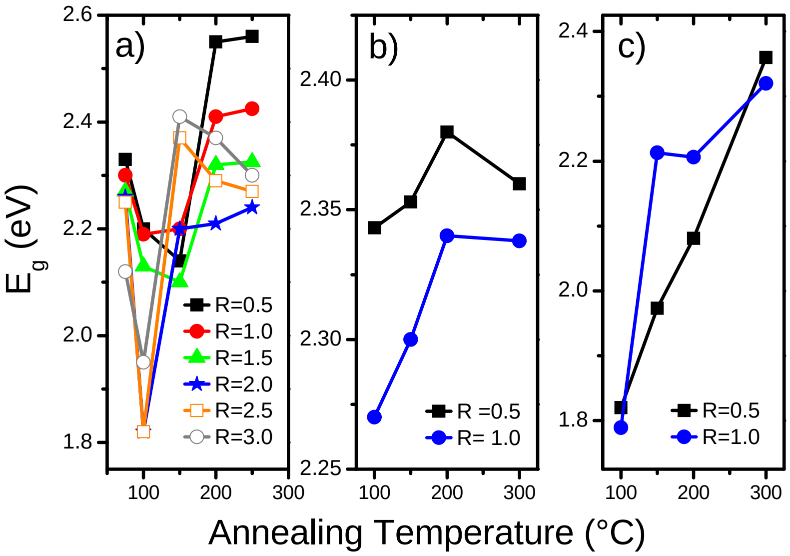

Fig. 2 Dependence of the band gap with the [Cu]/[S] ratio and annealing temperature, a) annealed in air, b) nitrogen and c) vacuum atmosphere respectively.

Copper sulfide has 23 vibrations modes. Eight of them are Raman active modes $2A_{1g}+2E_{1g}+4E_{2g}$ [19]. Raman spectra of the copper sulfide thin films annealed at 100 and 150 °C in an air atmosphere and with R = 0.5 and 1.0 ratios are shown in the Figure 3 a) and b). A strong peak at 474 cm^{-1} for the films annealed at 100 °C was identified as the CuS phase and for the thin films annealed at 150 °C the peak at 471 cm^{-1} corresponded to the Cu_2S phase. Analogous results have been obtained by others groups [19-24]. At 150 °C annealing temperature we obtained the Cu_2S which phase could be due to the decreasing of sulfur with the annealing temperature and the formation of a phase rich in copper. All the films were nanocrystalline in nature because of the temperature of the growth in the Chemical bath at 40 °C independently of the annealing atmosphere and temperature (75 to 300 ºC). The Raman spectra of the copper sulfide thin films annealed at 150 and 200 °C in nitrogen atmosphere and with R = 0.5 and 1.0 ratio are shown in the Figure 3 c) and d), and the films annealed in vacuum atmosphere are presented in the Figure 3 e) and f) with R= 0.5 and 1.0. A strong peak at 474 cm^{-1} for the films annealed at 150 °C was identified as the CuS phase and for the thin films annealed at 200 °C the peak at 464 cm^{-1} corresponded at the Cu_2S phase. In all atmospheres the bands 471 and 464 cm^{-1} correspond a S-S stretching, the others bands observed at 200, 267 and 921 cm^{-1} could be attributed to Cu-S stretching. This observation suggested that the anomalous behavior of this lowest frequency peak was related to the phase transition in Cu_2S to more amorphous phase with a shift of the principal peak at 464 cm^{-1}. The band at 464 cm^{-1} indicated that it was related to the S-S stretching of an intermediate between chalcocite and covellite. Since S-S linkages did not occur until covellitic structures from it was therefore concluded that the Raman bands observed at lower wavenumbers than for normal chalcocite were from a copper rich phase [25].

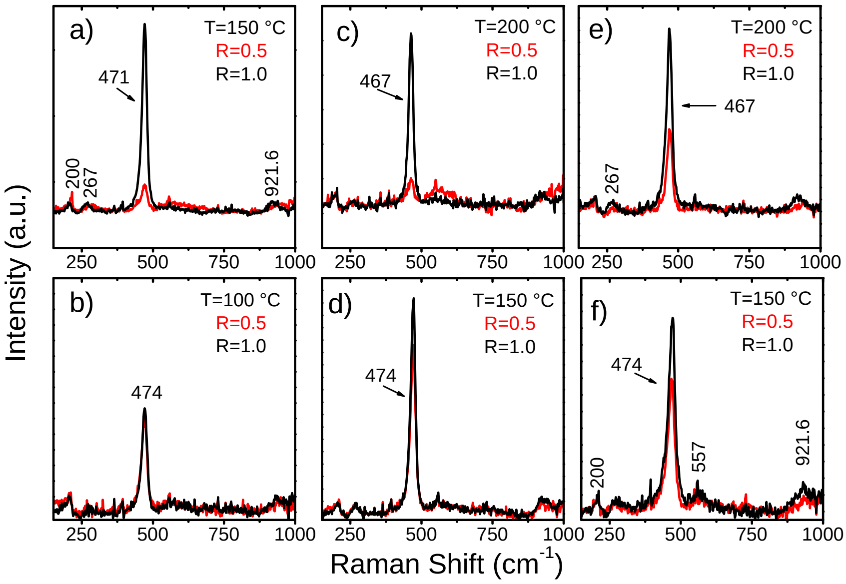

Figure 3 Raman spectra of the copper sulfide thin films annealed at 100, 150 and 200 °C with R = 0.5 and 1: Annealed in a), b) air, c), d) nitrogen, e), f) vacuum atmosphere respectively.

Table I show the EDS results for a [Cu]/[S] ratios 0.5 and 1 of the Cu_xS thin films deposited at 40 °C and annealed in air, nitrogen and vacuum atmospheres at 100, 150 and 200 °C. The films annealed in air exhibited a decrease of the [Cu]/[S] ratio with the increase of annealed temperature. For the ratio equal to 0.5, independent of the annealed temperature the films are close to the Cu_2S stoichiometry, the 1.0 ratio showed more deviation to the stoichiometry (Cu_2S) phase with loss of the sulfur compound with the increase of the temperature. In this atmosphere we obtain principally Cu_2S and $Cu_{1.97}S$ phases for a R= 0.5 and Cu_2S and $Cu_{1.8}S$ for a R= 1. In the case of the films annealed in nitrogen atmosphere at 100, 150 and 200 °C, the films exhibited an increase of the [Cu]/[S] ratio with the increase of annealed temperature. Two films with [Cu]/[S] ratios equals to 0.5 and 1 annealed at 100 and 150 °C respectively are close to the Cu_2S stoichiometry. The films increased the copper concentration with the increase of the annealing temperature. In this atmosphere we obtain principally Cu_2S and $Cu_{1.97}S$ phases. For the films that annealed in vacuum atmosphere, the films exhibited an increase of the [Cu]/[S] ratio with the increase of annealed temperature. The films with R= 0.5 are close to the Cu_2S stoichiometry. The films increase the copper concentration with the increase of the annealing temperature. The films with R=1.0 at 100 and 150 °C have deficiency of copper and for 200 °C had a deficiency of sulfur. The EDS results confirm that the samples have the Chalcocite phase. In this atmosphere we obtain principally Cu_2S, $Cu_{1.97}S$ for a R= 0.5 and Cu_2S, $Cu_{1.97}S$ and $Cu_{1.8}S$ phases for a R=1.

Table I. EDS analysis of the Cu_xS thin films as a function of the annealed temperature and atmospheres.

T (°C)	ATMOSPHERE					
	Air		Nitrogen		Vacuum	
CBD	R=0.5	R=1	R=0.5	R=1	R=0.5	R=1
EDS	[Cu]/[S]					
100	2.100	2.313	1.994	1.868	1.995	1.870
150	1.990	1.849	2.138	1.969	1.969	1.925
200	1.950	1.802	2.150	2.087	2.087	2.064

In order to study the surface morphology the films were examined by the SEM technique. In the Figure 4 show de SEM images for R=1.0 and 30,000 X for air annealed temperatures Figure 4 a) 100 ºC and Fig 4 b) 150 °C. Nitrogen atmosphere Fig 4 c) 150 ºC and Fig 4 d) 200 ºC and in vacuum atmosphere Fig 4 e) 200 ºC and Fig 4f) 300 ºC. The films annealed in air atmosphere presents a non-homogeneous aggregates, in the film annealed at 100 ºC we can observed more evident the non-homogeneity, the size of the aggregates varying of the 50-200 nm approximately. The films annealed in nitrogen atmosphere present the size of aggregates small and homogeneous in the order of the 50-100 nm no existing significance change with the annealing temperature. The films annealed in a vacuum atmosphere are homogenous, dense and free of pinholes. With the increase of the temperature we can observe a recrystallization with acicular aggregates. All the samples are composed for aggregates of the Cu_2S, $Cu_{1.97}S$ and $Cu_{1.8}S$ nanoparticles in the range of 50-200 nm.

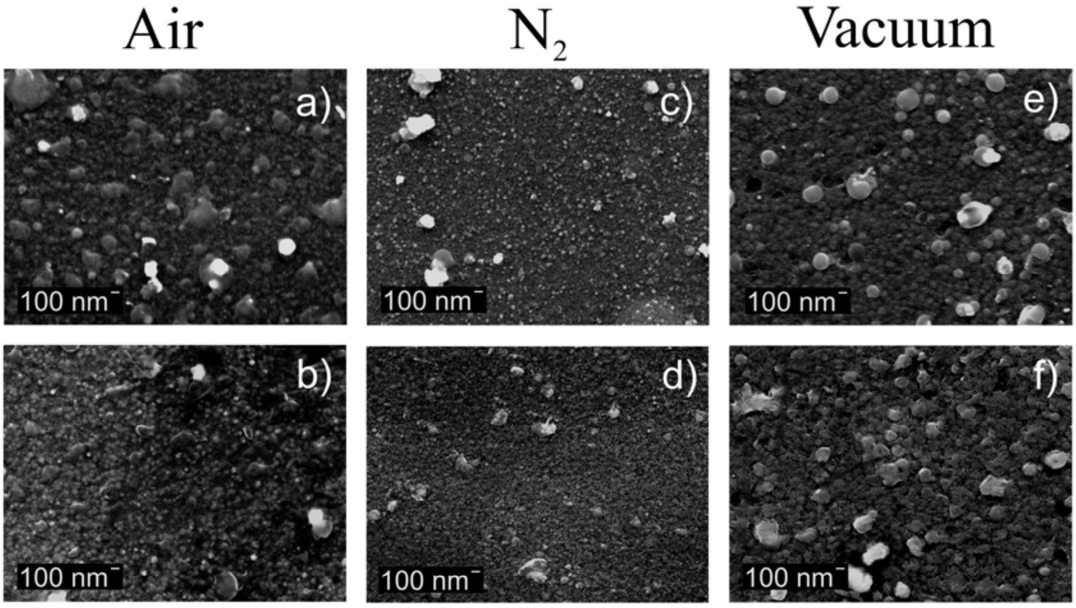

Fig. 4 SEM images of obtained Cu_xS films with R=1.0 and 30,000 x. a) Air 100 °C, b) Air 150 °C, c) Nitrogen 150 °C, d) Nitrogen 200 °C, e) Vacuum 200°C and f) Vacuum 300 °C.

The resistivity values of the Cu_xS samples are shown in the Figure 5 a), air b) nitrogen and c) vacuum atmospheres. For films annealed in air atmosphere the minimum values of resistivity are for R = 0.5 and 1 with annealed temperature of the 100 ºC, with resistivity values of the 2.2x10^{-3} and 2.66x10^{-3} Ω-cm respectively and for R=1 annealed in air at 150 °C the resistivity value of the 1.89x10^{-3} Ω-cm this is the minimum value reach with air atmosphere. This could be due to of the copper content in the samples, the copper content could be confirm with the EDS results where the [Cu]/[S] atomic concentration for the R= 0.5, 1 annealed at 100 °C and R=1 annealed at 150 °C, are 2.1, 2.3 and 1.85 respectively.

The resistivity values increase with the increase of temperature. The increase of the resistivity of the copper sulfide thin films could be due to the oxidation of the films or formation of oxide compounds with resistivity values higher than Cu_2S. In the Figure 5 b) we observed the resistivity values as a function of annealed temperature in nitrogen atmosphere. The resistivity values varying from 1x10^{-2} up to 2x10^{-3} Ω-cm for R=0.5 and 1.28x10^{-2} up to 1.24x10^{-3} Ω-cm for R=1. In both ratios (0.5 and 1.0) the resistivity values decrease with the annealed temperature (100-200 °C), after 200 °C the resistivity increases. This could be due to a greater sulfur deficiency and a possible oxidation of Cu_2S film. The minimum values are for R=0.5 and 1.0 both at 200 °C annealed temperature in nitrogen atmosphere with 2x10^{-3} and 1.24x10^{-3} Ω-cm values respectively. These two samples correspond to the highest concentration of copper in the films with respect to the EDS results.

The resistivity values as a function of the annealing temperature in vacuum atmosphere of the Cu_xS samples are shown in the Figure 5 c). The resistivity value varied from 6.76x10^{-2} up to 1.4x10^{-3} Ω-cm for R=0.5 and 1.77x10^{-1} up to 7.26x10^{-4} Ω-cm for R=1. In both ratios the resistivity values decrease with the annealing temperature except for the 300 °C with R=1 where the resistivity value increases. This could be due to the copper concentration that increases in respect to EDS results. The film at 300 °C and R=1 could have a possible deficiency of sulfur and oxidation of Cu_xS film. The minimum values are for R=0.5 and 300 °C with resistivity values of 1.4x10^{-3} Ω-cm and R=1.0 and 200 °C annealed temperature in vacuum atmosphere with 7.26x10^{-4} Ω-cm (Cu_2S). These values correspond to the lower resistivity values in the three different atmospheres studied in this work.

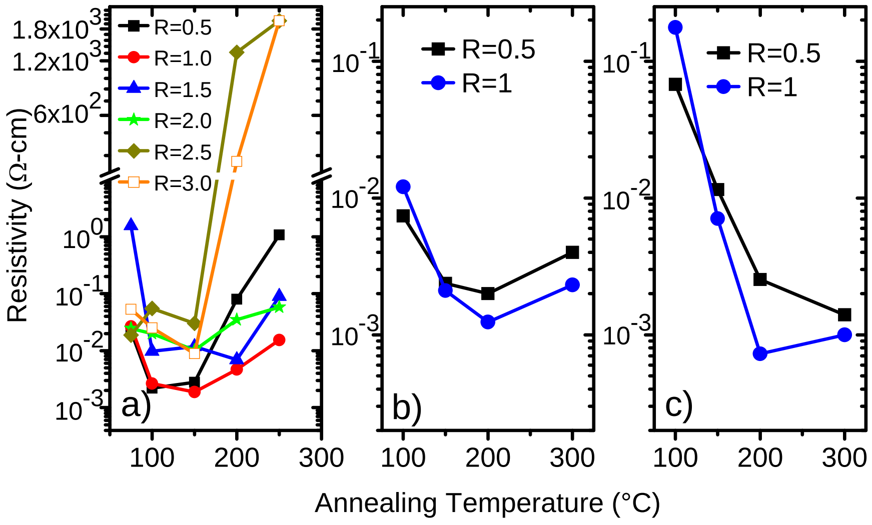

Fig. 5 Resistivity values of the Cu_xS samples varying the ratio and the annealed temperature. Annealed in a) air, b) nitrogen and c) vacuum atmospheres.

4. Conclusions

Cu_xS thin films have been grown by the Chemical bath deposition technique at 40 ºC and post treated in air, nitrogen and vacuum atmosphere were studied. All the films presented nano crystalline structure. The band gaps are in the order to 1.8 to 2.4 eV. The EDS results showed three different phases of the copper sulfide, identified as Cu_2S, $Cu_{1.97}S$ and $Cu_{1.8}S$, which are dependent on the annealing temperature and atmosphere. The resistivity value for the thermal treatment at

200 ºC and R= 1 and vacuum atmosphere treating is 7.26×10^{-4} Ω-cm that corresponds to Cu_2S phase.

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