Chalcogenide Letters Vol. 10, No. 12, December 2013, p. 543 - 553

EFFECTS OF THE ANNEALING ON CuS THIN FILMS USING TRIETHANOLAMINE AS COMPLEXING AGENT BY CBD

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We present the annealing effects on ammonia-free CuxS thin films using Triethanolamine and barium hydroxide as ligand agents by chemical bath deposition method. We synthesize two different samples: one as ground and the other with thermal treatment at 180°C. The X-ray diffraction showed an amorphous nature for both samples. It was established from reflection and transmission measurements that the direct energy band gap obtained was 2.57 eV as ground and 2.52 eV for annealing samples and the indirect energy band gap obtained was 1.365 eV as ground and 0.98 eV for annealing. The morphology was studied by Atomic Force Microscopy, where we obtained roughnesses of 19.128 nm and 23.506 nm for the thin films without and with thermal treatment, respectively; and the cluster sizes, which were between 87 − 200 nm ranges as ground sample and 136 − 247 nm range for annealed sample. The CuS (covellite) with amorphous structure was obtained. The resistivity of $\rho \cong 10 - 3\ \Omega$ cm was measured using Four Point Method. The chemical element composition was obtained by using XRay Photoelectron Spectroscopy. Complementary characterization of Raman Spectroscopy and Transmission Electron Microscopy were carried out.

(Received August 28, 2013; Accepted December 3, 2013)

Keywords: Triethanolamine, Complexing Agent, Annealing, Chemical Bath Deposition, Thin Film

1. Introduction

Cu_xS thin films attract the attention of many researchers due to their interesting optical and electrical properties in photovoltaic applications as pigments, semiconductors, fluorescent fixtures and even superconducting[1,2]. It is known that Cu_xS are useful minerals and their mineralogical and technological properties have been studied extensively[3]. The compound exhibits fast ion conduction at higher temperatures and exists in a wide variety of compositions ranging from Cu_2S at the cooper-deficient sites such as CuS [4,5], $Cu_{1.76}S$, $Cu_{1.96}S$ [6], and $Cu_{1.8}S$ [7]. Copper sulfide (Cu_xS, x=1.8–2) thin films, mainly Cu_2S [8], are considered promising materials for solar energy conversion systems, especially as p-type semiconductors and/or absorbers of visible light, due to their structural, electrical and optical properties. These properties are often determined by the composition of Cu_xS that, in turn, is dependent on the precursor solution composition and deposition parameters[9]. The superiority of a chemical bath deposition technique (also called as

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growth solution) lies in the advantages of having a variety of substrates (insulators, semiconductors and metals) for deposition, a large surface area, simplicity, and lower cost[10,11]. One purpose of the present paper is to further the study in the features of CuS as ground and thermally annealed recently developed in our research group[12], focusing in the chemical composition, optical and electrical properties. Also, other workgroups have deposited CuS by Chemical Bath Deposition[13], in order to keep low temperature processing.

3. Materials and methods

The CuS thin films were obtained from an aqueous solution mixture that was compound by 31 ml of H_2O, 2 ml of cooper nitrate (0.1 M), 2 ml of barium hydroxide (0.01 M), 2 ml of triethanolamine (1M), 4 ml of thiourea (1 M) and 19 ml of H_2O. See reference 12 for details.

The reaction conditions to get the CuS thin films were a bath with a temperature of 60°C and reaction time of 15 min., these films presented a green-gray translucent color, the adhesion of the film is not too strong, and the obtained thicknesses of the films were of 150 nm approximately. The annealing was applied to the CuS thin films at 250 to 450°C for 30 minutes, all samples suffered complete evaporation leaving only the substrate, but when the condition was of 180°C for 15 minutes the optimum annealing temperature was achieved. The adjusted annealing temperature was 180°C, remaining amorphous after the annealing.

The X-ray diffraction measurements were performed using a Rigaku Ultima III diffractometer. Optical transmission spectra were recorded by an Ocean Optics USB4000-UV-VIS spectrometer in the 280-850 nm wavelength range. The morphology of the samples surface was obtained by Atomic force microscopy (AFM) using a JSPM-4210 scanning probe microscope (JEOL Ltd). Chemical composition was done in a Perkin-Elmer PHI 5100 XPS and the Raman dispersion was performed by Micro-Raman X'Plora BXT40.

4. Results and discussion

The XRD spectra of CuS thin films are shown in the Fig. 1. The diffraction patterns as ground and the annealing samples are amorphous. Nevertheless, as can be observed in the superior graph, the behavior remains amorphous after the thermal process; this was carried out in presence of environmental conditions. We do not discard the possibility that the films contain Nano scale structures.

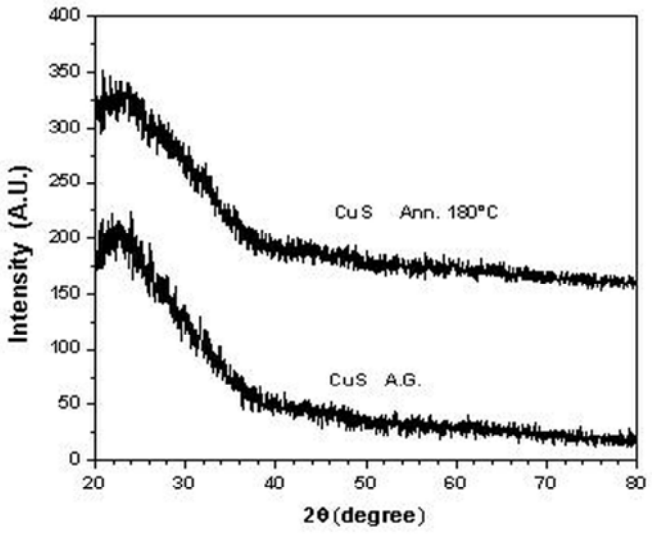

Fig. 1. X-ray diffraction pattern of the different CuS thin films.

The Fig. 2 shows the curves of transmittance and reflectance for both samples, as are labeled in the figure. The transmissions are good enough in both cases, the as ground sample being slightly higher. The reflectance behaviors are inverses with intensities between 4-11% ranges.

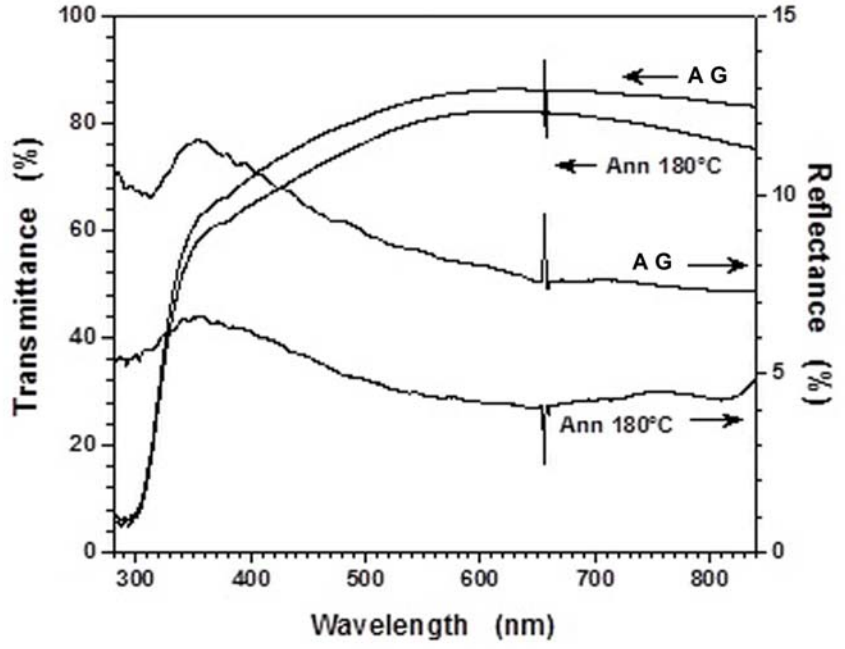

Fig. 2. Transmittance and Reflectance versus wavelength of CuS thin films as ground and annealing samples as indicated in the plots.

The Fig. 3 and Fig. 4, present the graphic foundation for the direct energy band gap calculations for the as ground and annealing thin films, respectively. The energy band gap obtained was 2.57 eV for as ground and 2.52 eV for annealing samples. The resulting differences between the energy band gap values are in concordance with increment of grain size supposed by the annealing.

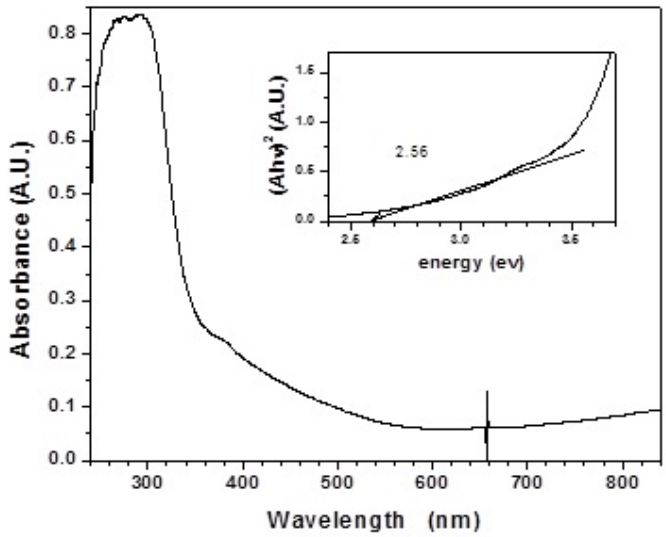

Fig. 3. Absorbance versus Wavelength for as ground CuS thin film. The inset plots the square optical absorption times energy versus energy.

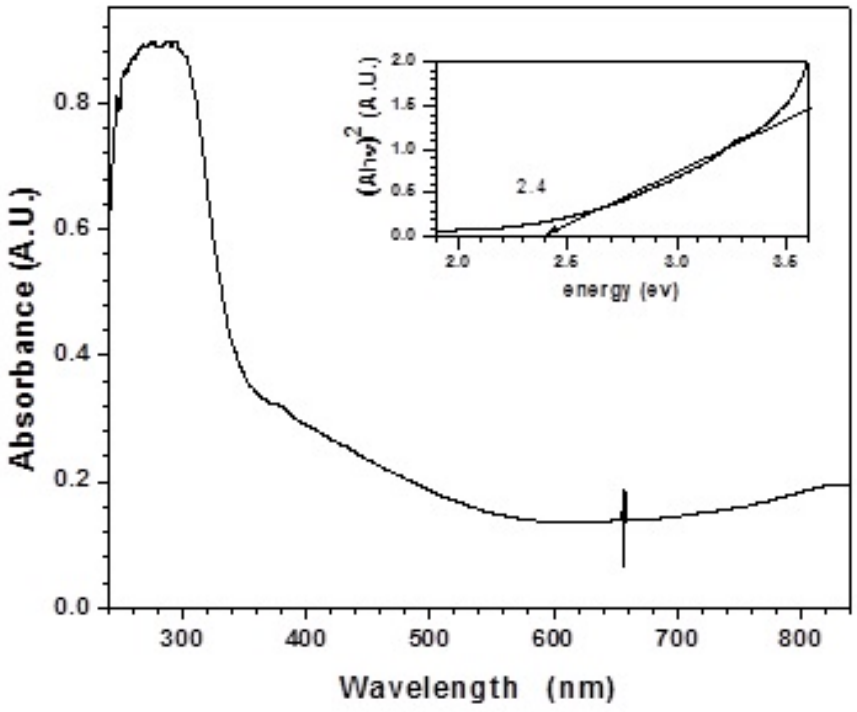

Fig. 4. Absorbance versus Wavelength for annealing 180°C CuS thin film. The inset plots the square optical absorption times energy versus energy.

The Fig. 5 and Fig. 6 are the geometric fundament for the indirect energy band gap calculations for the as ground and annealing thin films, respectively. The energy band gap obtained was 1.365 eV for as ground and 0.98 eV for annealing.

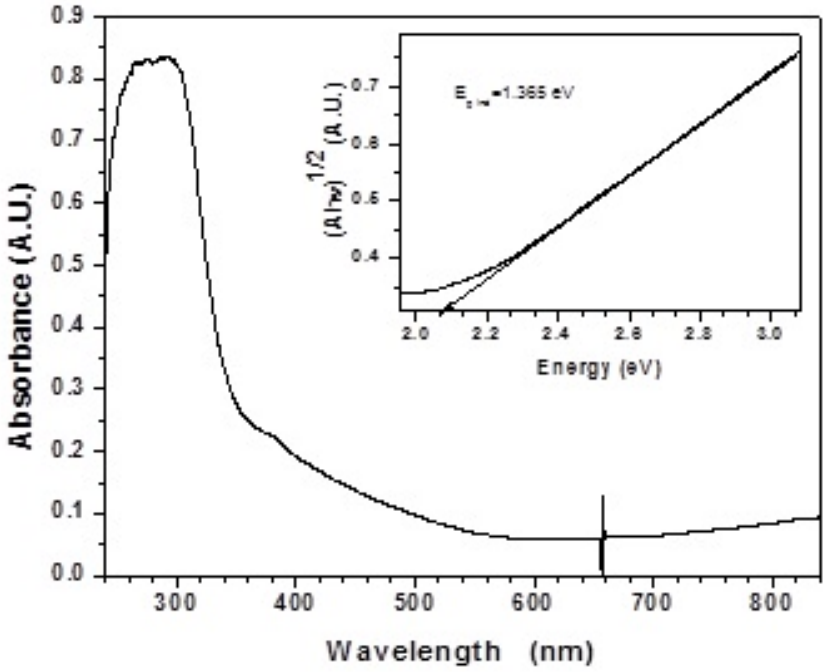

Fig. 5. Absorbance versus Wavelength for as ground CuS thin film. The inset plots the square root of optical absorption times energy versus energy.

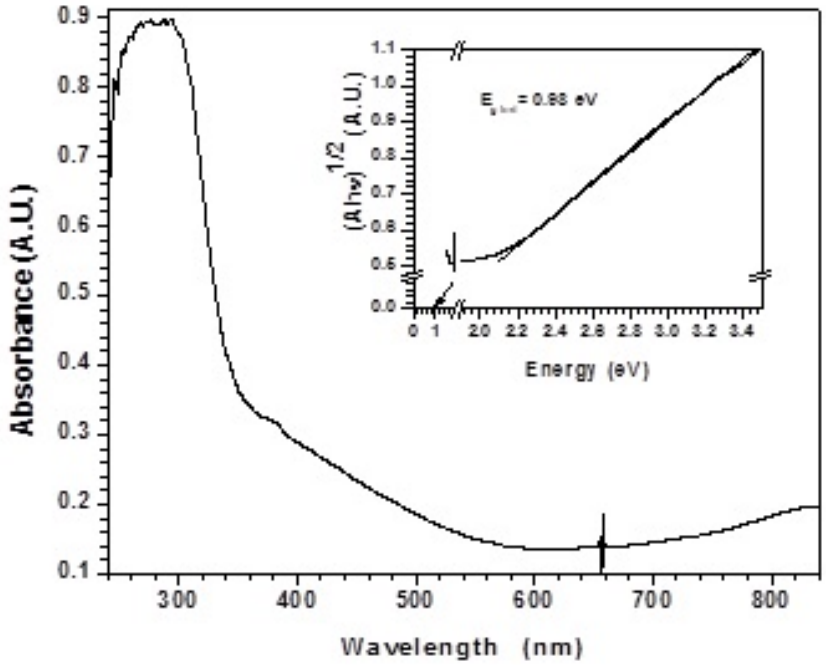

Fig. 6. Absorbance versus Wavelength for annealing 180°C CuS thin film. The insets plot the square root of optical absorption times energy versus energy.

The morphology was obtained by Atomic Force Microscopy. Fig. 7 shows the surface of CuS thin film as ground from two different views, perspective and top, the roughness can be observed, using the software[14], giving an rms value of 19.128 nm. The peaks in the image should correspond to amorphous grains sets, which could be formed by nanoparticles.

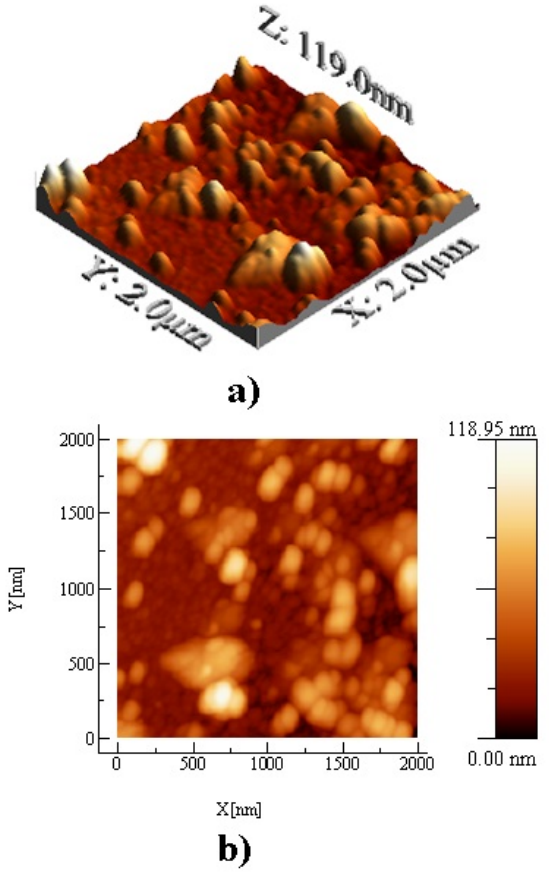

Fig. 7. Atomic Force Microscopy for as ground CuS thin film: a) Perspective and b) Top view.

The Fig. 8 presents a similar study, but corresponding to the CuS thin film with annealing at 180°C for 15 minutes, also in two different views, perspective and top. In this case the rms roughness using the software was 23.506 nm. Indeed, the peaks in the image must also correspond to amorphous grain sets, but we suppose there were coalescence due to the annealing.

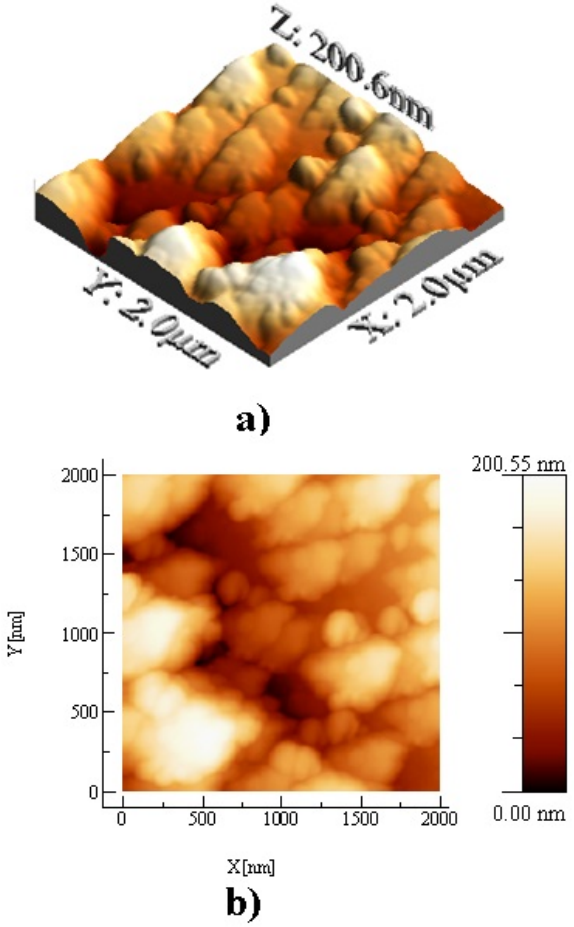

Fig. 8. Atomic Force Microscopy for annealing 180°C CuS thin film: a) Perspective and b) Top view.

The resistivity was calculated using the four dots method; we deposit 4 lineal contacts of silver on the top of the film. By the other hand, 1 volt was applied in the two internal contacts using a voltage source. While, in the external contacts was measured the resultant current, and the bulk resistivity was calculated by the next expression

$$\rho = \frac{\pi}{\ln(2)} t\left(\frac{V}{I}\right) = 4.523t\left(\frac{V}{I}\right) \tag{1}$$

Where t is the film thickness in cm, V represents the applied voltage and I the current measured. The resistivity value was of 5.39 x10-7 Ω*cm and 1.94 x10-7 Ω*cm for as ground and annealing thin film, respectively.

The Raman spectroscopic characterization shown that the materials fit in all the peaks to the Covellite mineral according to the database rruff covellite R060306[15], this indicates a stoichiometric combination of copper and sulfur for both samples. Fig. 9 presents the Raman spectroscopy for CuS thin films, the dashed and solid lines represent the as ground and annealing thin film, correspondingly. As can be observed in the inset the thermal annealing leads to a shift of the main peak, which can be interpreted as a structural change through the coalescence or looseness of the nanoparticles.

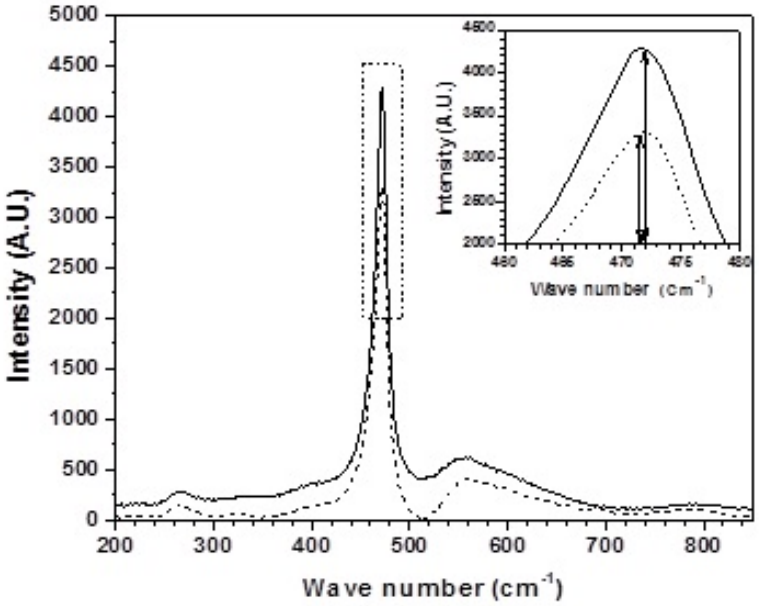

Fig. 9. Raman Spectroscopy for CuS thin films, the dashed and solid lines represent the as ground and annealing thin film, correspondingly. The inset shows an enlargement of selected area.

The X-Ray Photoelectrons Spectroscopy gives the resulting material chemical composition. These results can be seen in the Fig. 10, which compares the spectra for both samples labeled. In Table I a correlation among the peaks, the corresponding elements and the quantum energy levels involved. Combining Fig. 10 and Table 1, we conclude the elemental composition of the CuS films associated to binding energies of the different phases. For CuS the peaks 1, 2, 6, 11 and 13 are associated with copper, the 9 peak corresponds to the sulfur state. It is important to note that the peak labeled with 5 could not be identified. Obviously, carbon and oxygen are present because the samples were carried out in normal atmosphere and the measured was done without surface etching.

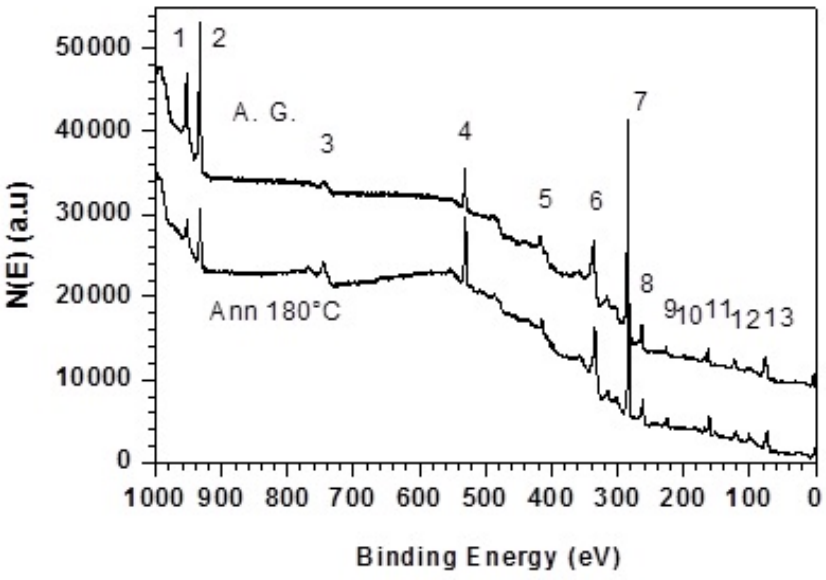

Fig. 10. X-Ray Photoelectrons Spectroscopy spectra for CuS thin films as ground (A.G.) and annealing (Ann 180°C).

Table 1. Correlation of CuS XPS spectra, elements and quantum energy levels.

XPS of CuS	
1	Cu 2p1
2	Cu 2p3
3	O KLL (Auger)
4	O 1s
5	-
6	Cu LMM (Auger)
7	C 1s
8	Cl 2s
9	S 2p
10	Si 2s
11	Cu 3s
12	Si 2p
13	Cu 3p3

In Fig. 11, the High Resolution Transmission Electronic Microscopy (HRTEM) characterization is presented where the electron diffraction patterns of CuS thin film annealing can be observed. The a) and b) parts are with less enlargement than the c) and d) parts, as can be seen, in Fig. 11. The a) subsection corresponds to the as ground CuS thin film, while the b) subsection is for the annealed CuS thin film. In both images a granular structure can be observed, but more compact for the annealed sample. In the same first two pictures we can observe crystals of sizes around of 6nm. Indeed, the c) and d) subsections present the HRTEM with mark resolution of 5 nm, were an interplane distance of 3.21Å that corresponds to the (111) plane of CuS is displayed. In Fig. 12 the Fourier transform of the annealing thin film is showed and a list of interplanar distances calculated and compared with the JSPDS-01-074-1234 reference[16] for the copper sulphide are displayed in the Table 2, the shown concordance is quite acceptable.

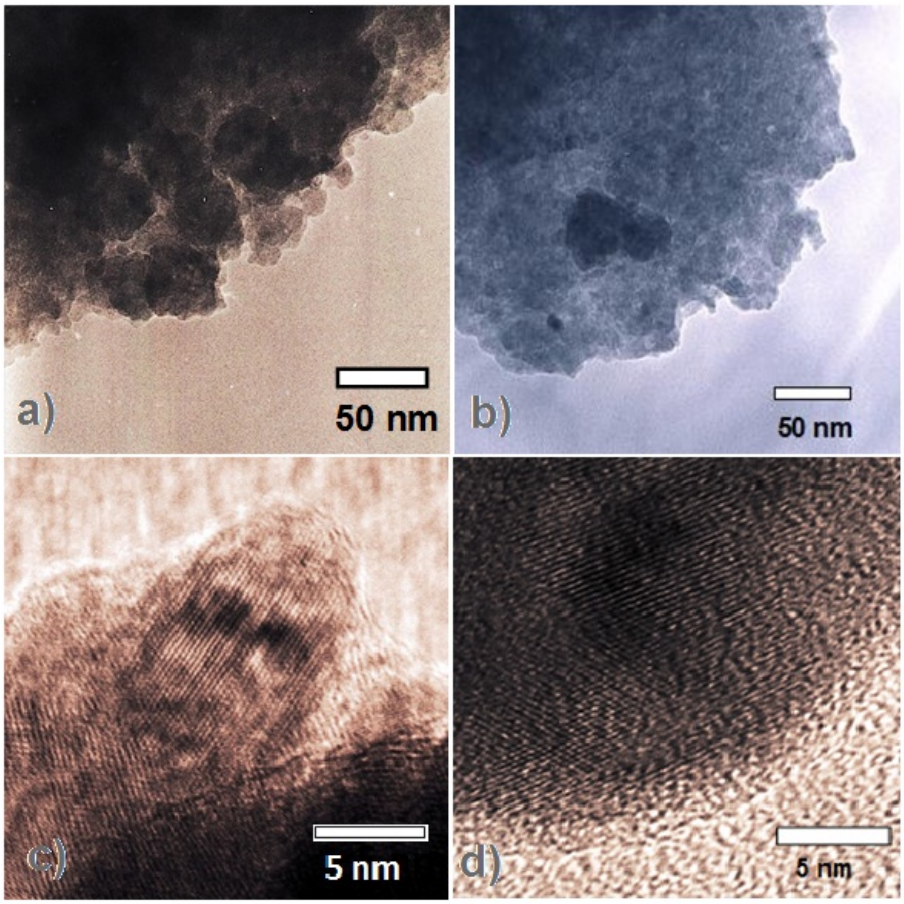

Fig. 11. High Resolution Transmission Electron Micoscopy CuS thin film a) and c) for as ground sample, and b) and d) for annealing sample.

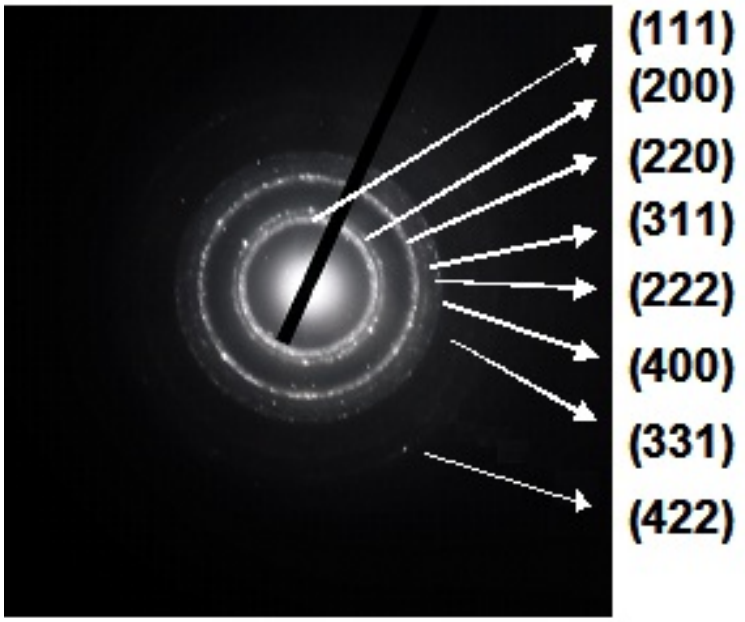

Fig. 12. Electron Diffraction pattern for CuS annealing thin film

Table 2. Correlation of CuS XPS spectra, elements and quantum energy levels.

Interplane Distance	
Calculated (Å)	CuS(Å) JSPDS-01-074-1234
3.174	3.217
2.763	2.811
1.878	1.895
1.696	1.632
1.619	1.588
1.515	1.455
1.342	1.353
1.204	1.257
1.092	1.157

5. Conclusions

In this work we show the effects of annealing on CuS thin films using triethanolamine and barium hydroxide as complexing agents by chemical bath deposition technique. These films present an amorphous behavior when analyzed by XRD but when analyzed by HRTEM shown a granular structure composed by CuS nanoparticles which diffract an electron beam. The AFM study shows the grain sets coalescence of CuS when the films are thermal annealed at 180°C during 15 minutes. The chemical composition was corroborated by XPS analysis in agreement with the expected.

Acknowledgments

We want to give thanks to Roberto Mora Monroy for the technical support in the XPS measurements, Dr. Tom Piters for his help in the resistivity measurements, Dr. Rogelio Gamez Corrales because the Raman facilities, Dr. Miguel Valdez for the use of AFM equipment.

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