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SYNTHESIS OF COPPER SULFIDE (CuS) THIN FILMS BY A SOLID-VAPOR REACTION

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Copper sulfide thin films were obtained by sulfidizing sputtered copper substrates through a simple solid-vapor reaction at 110°C for 3 h. The thin films were characterized by Small Angle X-Ray Diffraction, Field Emission Gun Scanning Electron Microscopy, X-Ray Photo Electron Spectroscopy and Raman Spectroscopy. Films are made of hexagonal Covellite (CuS) phase. Thickness of the films varies from 70 to 110 nm. A granular to smooth morphology transition is seen with thicker initial sputtered copper deposits. Optical properties were determined by UV-VIS Spectroscopy. Semiconductor behavior was observed with band gaps ranging from 2.05 to 2.25 eV depending mainly on the films thickness.

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1. Introduction

There is great interest on the development of low cost and non-toxic materials for solar energy conversion and storage. Copper sulfides thin films have received special attention for such applications because they are low cost and non-toxic and they exhibit important photovoltaic and photocatalytic properties [1, 2]. Copper sulfides are p-type semiconductors which have various stoichiometric forms that are stable at room temperature, ranging from sulfur rich (CuS) to copper rich (Cu_2S) [3-7]. The band gaps of CuxS thin films are reported in the range of 1.2 to 2.6 eV but these values can vary according the calculation method [8-13]. Relatively low material requirement, low energy intensive process and possible use of flexible coatings are some of the benefits of thin film solar cells [14]. Copper sulfides thin films, especially CuS films, have proven to exhibit favorable materials characteristic for solar cells applications. Kim et al. [15] reported superior performance and stability of covellite films used as counter electrodes in QDSSCs compared with other copper sulfide phases. Also, a promising behavior of CuS as counter electrode in bifacial quantum dot-sensitized solar cells has been reported. [16].

Several synthesis methods to deposit thin film of copper sulfides have been developed such as chemical bath deposition, hydrothermal, photochemical deposition, vacuum evaporation, electro-deposition, electroless chemical deposition, spray pyrolysis, solvotermics, sputtering, thermal oxidation and sol gel method among others [13, 17-22]. Some disadvantages that these methods could have are high temperature, large by-products formation or the need of annealing treatments after deposition at temperatures that difficult their application in flexible polymeric substrates. The aim of this work is to synthesize CuS thin films by using a methodology that can be attractive due to its low cost, low processing temperature (110 ^oC) and low by products formation. It combines copper sputtering on substrates and a simple solid-vapor reaction during 3

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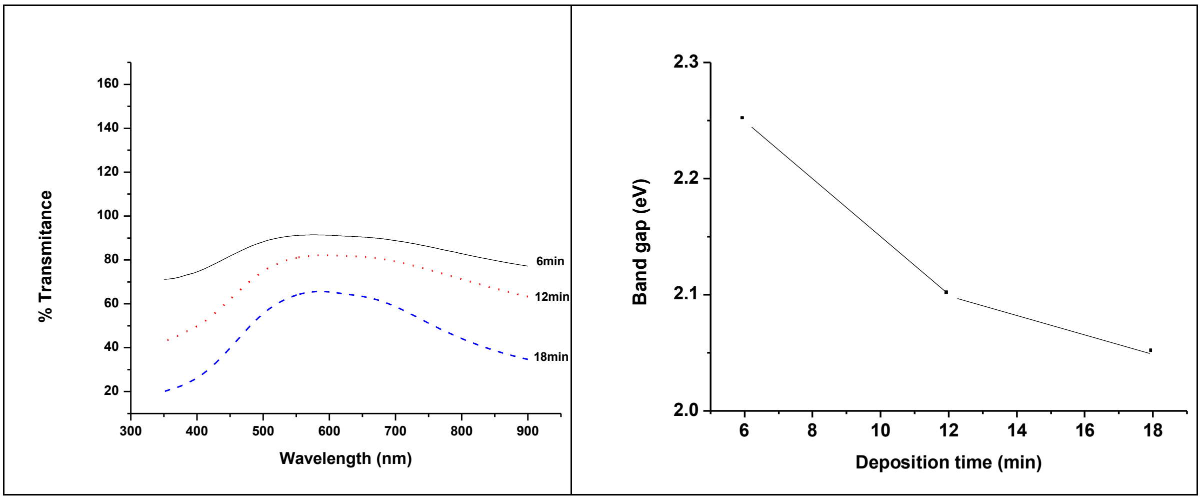
h in a glass container at atmospheric pressure and 110 °C. Ke et al. in 2014 [16] reported the synthesis of CuS nanosheets for DSSC using a similar methodology except that they use an autoclave at 60 °C during 12 hr.

2. Experimental details

Copper films were deposited on glass substrates during 6, 12 and 18 minutes by plasma sputtering using a copper target (99.99% Cu, Ted Pella 91117) and a current of 20 mA. The films thickness was controlled by the sputtering time. Then, these films and two beakers with 20 mL of deionized water and 3 g of sublimed sulfur (99.97%, Fermont PQ09122) were placed into a glass container covered with aluminum foil. The reactants were used to generate a reactive sulfur atmosphere according to the international standard ASTM B809. The reaction's temperature was 110 °C during 3 h at atmospheric pressure. The obtained thin films were characterized by X-Ray Diffraction using CuKα radiation (XRD, X'Pert Pro PANalytical, λ = 0.1542 nm), Small Angle X-Ray Diffraction (Rigaku Ultima III X-ray diffractometer), Field Emission Gun Scanning Electron Microscopy (Jeol JSM-7000F), X-Ray Photo Electron Spectroscopy (Versa probe, Al k-alpha source) and Raman Spectroscopy (Raman Witec Alpha 300 RA). XPS and Raman spectra were deconvoluted using Peak Fit software (version 4.2). Films thickness was determined by cross sectional image analysis. The films optical properties were also determined by UV-VIS Spectroscopy (Perkin-Elmer Lambda 24 UV-Vis spectrophotometer).

3. Results and discussions

Figure 1a) shows the UV-VIS transmission spectra of the synthesized films. The films transmittance decreases with their thickness. The absorption edge of interest is found in the ranges of wavelengths from 441 to 448 nm where transmissions change drastically. Maximum transmittance is observed at wavelengths in the range of 500 nm to 700 nm. Grozdanov et al. [13] reported similar behavior for CuS films obtained by electroless chemical deposition.



a) b)

Fig. 1. a) Transmission spectra of the films; b) Relation between band gap values vs deposition time of the films.

The high transmittance in the visible light wavelength range of these films could help to improve the performance of DSSC cells if the films are employed as counter-electrodes. The cell could absorb light not only from the front but also from the rear side as reported by Ke et al. [16].

The band gaps of the films were obtained from the $(\alpha h\nu)^2$ vs hv graphs (Figure 1b)). Values are in the range of 2.05 to 2.25 and band gap decreases with the increment of the coating thickness. These values are within the wide range (between 1.2 to 2.6 eV) reported for Cu-S films calculated using the same methodology [8-13].

Fig. 2 and 3 show FE-SEM representative images of the thin film surfaces as well as the measured thickness of the transversal sections before and after sulfuration.

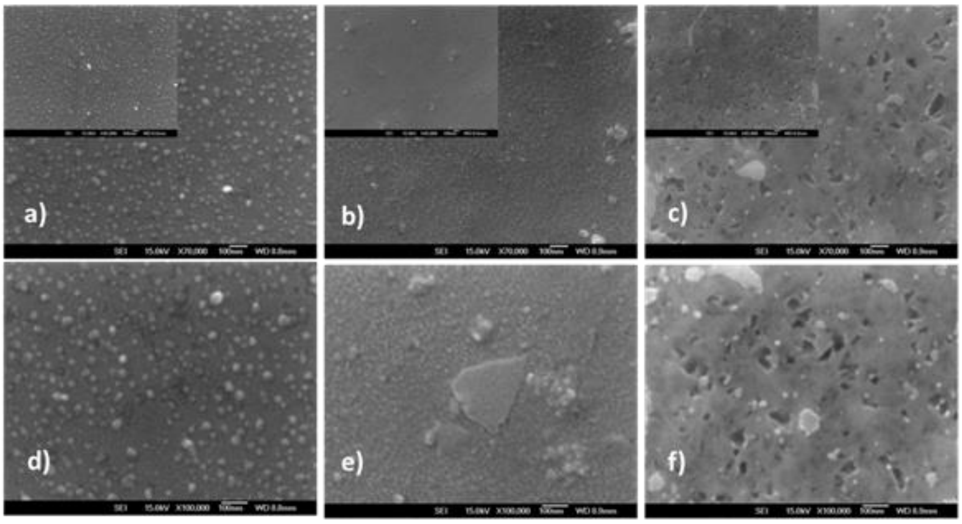


Fig. 2. FE-SEM representative images of the thin film surfaces. a) b) and c) correspond to 6,12 and 18min deposition time at low magnification; d), e) and f) 6,12 and 18 min deposition time at high magnification.

Sulfurized thin films are in the range of 70 to 110 nm. The surface morphology changes with the thickness of the copper layer deposited by sputtering. The samples with initial copper layers sputtered during 6 minutes (60 nm average thicknesses) show a granular morphology which combines fine and coarse grains. When the copper layer increases to 63 nm (12 minutes sputtering) the fine grains exhibit similar size but instead of coarse grains, smooth large areas are observed. When the initial copper layer is increased up to 70 nm (18 minutes sputtering), the surface morphology is smother but more porous. These morphology changes can be explained with the amount of copper available to diffuse and react with sulfur ions (S^{-2}) during the solid vapor reaction to form copper sulfide. If more copper is present, there is more diffusion and grow of copper sulfide in layers that produce a thicker structure. The proposed reaction and growing mechanism is similar to the one reported for the Ag-S system in our previous work [23]. Sulfur ions (S^{-2}) coming from the gas atmosphere react with the Cu ions (Cu^+) on the glass substrates to form copper sulfide CuS compounds. The continuous supply of sulfur ions to the atmosphere could produce a non-stable compound with contains Sulfur in excess (e.g. CuS_x) on the film surface. This compound can promote the diffusion of copper ions from inner layers trough the already formed copper sulfide. This diffused copper will react again with the atmosphere and a layer growth will occur. It is important to mention that at the reaction temperature (110°C), the water present in the system evaporates completely and could aid in the H_2S formation, a very reactive gas with copper that produce Cu_XS compound. Sulfuration of copper species by sulfur is non-dependant of water presence but it is known that it increases the speed of reaction [24, 25]. The films were obtained onto glass substrates but they could also be applied onto flexible substrates.

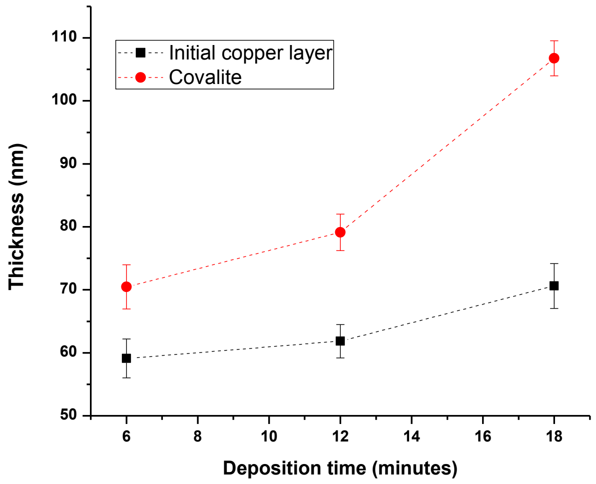


Fig. 3. Thickness of the samples transversal sections before and after sulfuration. Results are the average of at least three samples per condition.

X-Ray diffraction results are shown in Fig. 4. All samples were analyzed by XRD diffraction but they showed very small reflection peaks at 2 θ angles of 29.5, 31.8 and 48.1 . Therefore, small angle X-Ray diffraction was used (Figure 4 a).

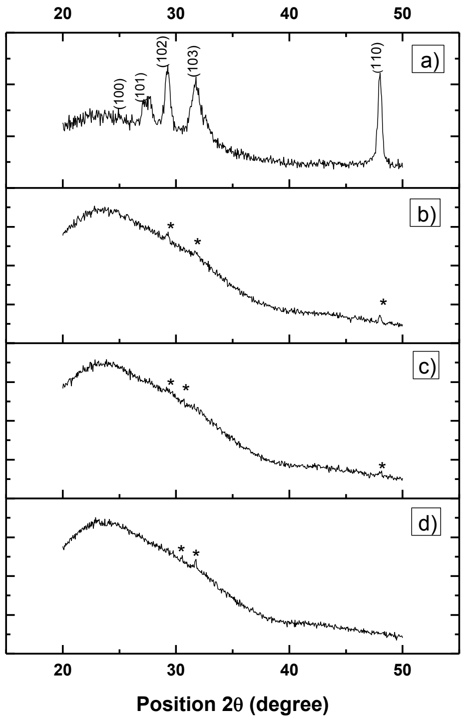


Fig. 4. XRD and Small angle XRD patterns. a) Small angle XRD pattern of 18 minutes sample, b), c) and d) XRD of 18, 12 and 6 minutes sputtered samples. (Solid-Vapor reaction time was 3h for all samples).

Hexagonal Covellite (CuS) space group P63/mmc, space group number 194 was the phase found on the samples and it was identified with the PDF card 01-078-0877 calculated from ICSD using POWD-12 of the PANanalytical X'pert PDF2 2003 database. The most intense peaks occurred at the same observed in the XRD spectrum of the 18 minutes samples (29.5, 31.8 and 48.1) and correspond to the reflections of the (102), (103), (110) planes. Additional reflections of the same phase were found at 2θ angles of 27.1, 27.6 and 32.8.

Raman spectrum is shown in Figure 5. The presence of well defined bands corroborates the films crystallinity. Crystalline products show sharp Raman peaks, meanwhile amorphous or polycrystalline materials exhibit broad peaks [26]. Well defined bands at 473.7-475 cm^{-1} is observed. This band is assigned to the S-S stretching mode of S_2 ions at the 4e sites of Covellite and it has been reported at 473 cm-1 by [27-29] and at 474 cm-1 by [30-33]. The rest of the contributions on the spectrum correspond to the glass substrate.

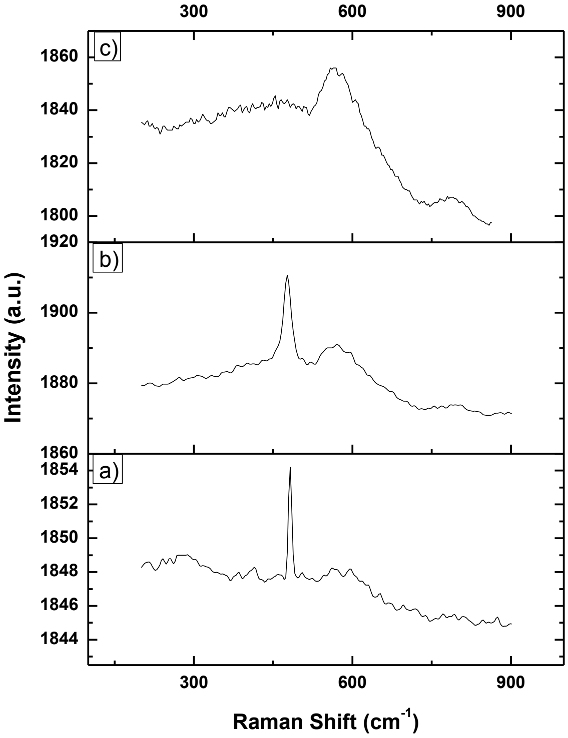


Fig. 5. Example of the Raman spectrum of the sulfurized samples. a) 6 min sputtered samples b) 18 min sputtered samples c) Glass substrate spectrum.

The films surface composition was characterized by XPS. Figure 6(a) shows the S2p peaks obtained by XPS of the copper sulfide films. Two doublets at 161.8 and 163.28 eV can be observed. The S2p2/3 at 161.8 eV is the binding energy related to the S-S sulfur bonds reported for Covellite (CuS) and the S2p2/3 presence at 163.28 eV can be related to a highly copper deficiently non stochimetric sulfide in the film [34]. The presence of a very weak peak is observed at 168.3 eV and could be attributed to sulfate presence (SO_4^{2-}) on the film surface [35]. The Cu 2p3/2 binding energy of the samples is shown in Figures 6 (b). The Cu 2p3/2 peak is found at 931.9 eV which agrees with the binding energy of copper in Covellite CuS [36].

The O 1s spectrum of the films is shown in Figures 6(c). Weak peaks are observed around 531.6 and 533.5 eV and they have been assigned to the presence of weakly absorbed ions of O^- of subsurface species in previous studies [37].

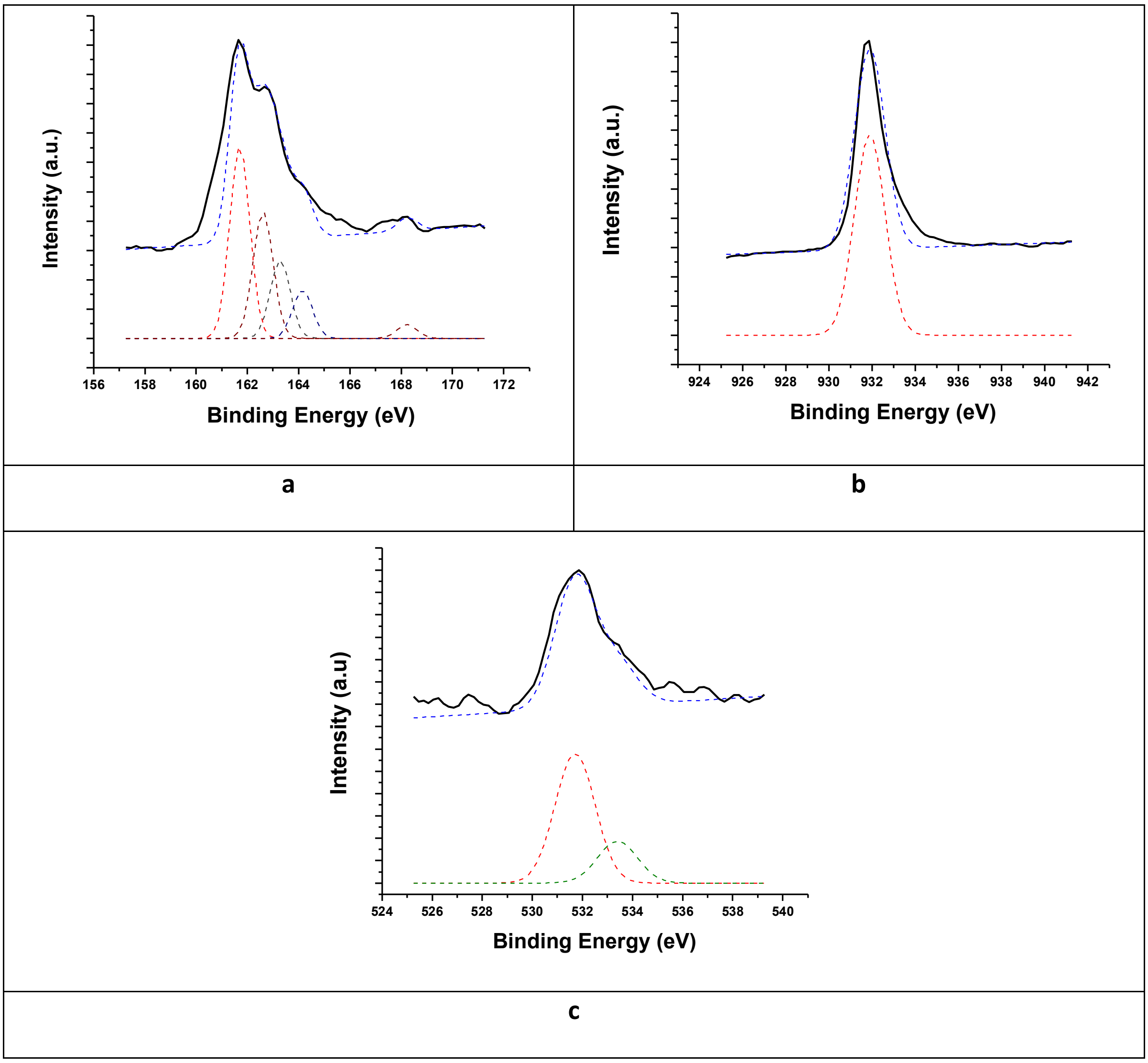


Fig. 6. XPS analysis of the sulfurized samples (18 minutes sputtered).
a) S2p b) Cu 2p3/2 c) O1s binding energies.

4. Conclusions

Copper sulfide (Covellite-CuS) thin films in the range of 70 to 110 nm were obtained, over glass substrates, using a simple method that combines sputtering and a solid-vapor reaction. Low cost, short reactions time, low processing temperature (110^{o}C) and low by products formation are advantages of this method.

The initial copper layer thicknesses affect the resulting films morphology as well as their transmittance. High transmittance in the visible light wavelength range was observed on the films. Band gaps mainly depend on the films thickness and are in the range from 2.05 to 2.25 eV (calculated from the $(\alpha hv)^2$ vs hv graphs). These material properties are very attractive for device including flexible electronics applications at low deposition temperature.

Acknowledgments

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