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# STUDY OF OPTICAL, MICROSTRUCTURAL AND ELECTRICAL PROPERTIES FOR MULTIPLE DIP DEPOSITION OF CuS FILMS PREPARED BY A SIMPLE CBD

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This work is focused on a systematic study of homogeneous growth of copper sulfide (CuS) thin films deposited under similar chemical deposition conditions and considering the variations of the number of dips during the chemical bath deposition process. The aim of this work is to investigate the influence on the structural, optical and electrical properties of CuS films when varying the deposition parameters aforementioned. The films were deposited at 27 °C during 45, 60, 75 and 90 minutes per dip. The CuS thin films presented an amorphous structure. The Raman spectra showed one band at 475 $cm^{-1}$ (Eg) which corresponds to the CuS vibration. These notable characteristics are preserved in the samples obtained from all dips. The energy band gap values are in the range from 1.65 to 2.6 eV, the former value corresponding to the three dip process. The conductivity of CuS films increased as the grain size increased. These characteristics in CuS films make them suitable candidate for various semiconductor device applications, obtained by a rapid and low- cost technique.

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*Keywords:* CuS, Multiple Dips, Thin Films, Chemical Bath Deposition

## 1. Introduction

Recent efforts to develop alternative inorganic routes to produce semiconductors have increased the interest of the scientific community. Over the years, CuS thin films exhibited a band gap in the range from 1.2 to 2.6 eV; however, these values can vary according the calculation method [8-13]. In particular CuS thin films have been demonstrated using various methods techniques as sputtering [1], thermal evaporation [2], spray pyrolysis[3], electrodeposition [4], and chemical bath deposition (CBD). Among these deposition methods, CBD is simple, inexpensive, reproducible, yielding uniform and adherent films deposited at low temperatures. Moreover, CBD offers a control on the film thickness during the deposition [5-6].

Nowadays, three approaches have been reported to deposit thin and thick chalcogenide films with good properties namely; simple chemical bath, where the important related parameter with the thickness is the deposition time [7]; the multiple dip approach where the substrate is

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repeatedly dipped in a fresh solution [8]; and the continuous dip approach, where the substrate remains in the reaction bath while the reactants are periodically replenished [9-10]. The latter enables studying the effect of the thickness, band gap, electrical behavior, and crystallite and grain size. To our knowledge, there is no previous report about the influence for multiple dip deposition of CuS thin films by CBD.

In the present work, the CBD process is applied to obtain CuS films with different thicknesses, band gap and crystallite size through a multiple dip approach. The deposited films were characterized with respect to their physical, optical, microstructural and electrical properties.

## 2. Experimental details

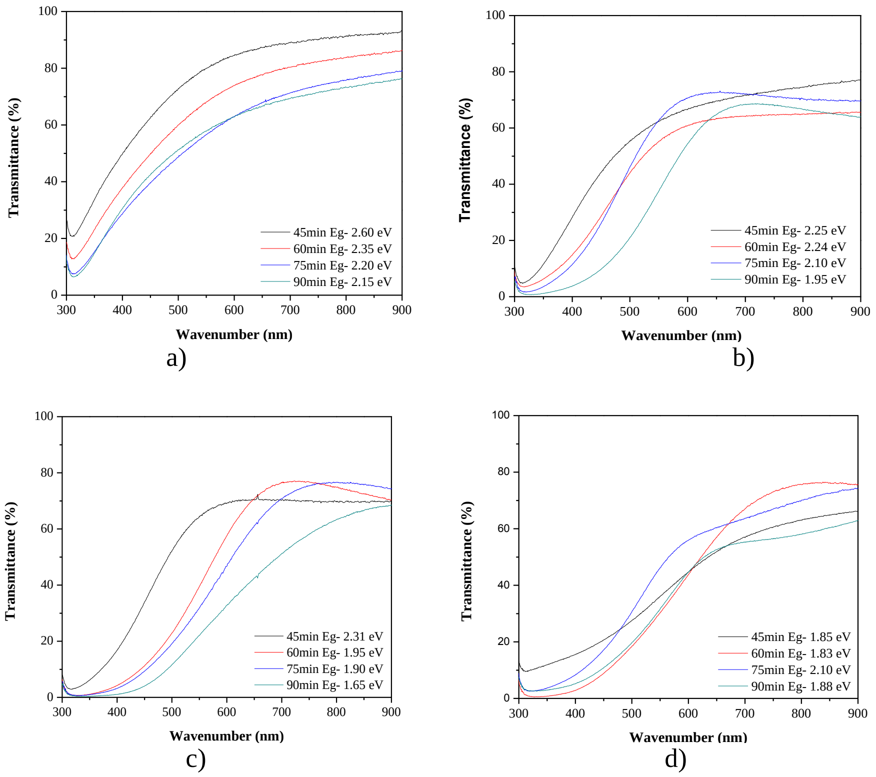
The CuS films were deposited by immersion of glass substrates in a CBD solution prepared from copper chloride ($Cu(NO_3)_2$), triethanolamine ($C_6H_{15}NO_3$), ammonia ($NH_4OH$) and thiourea ($SC(NH_2)_2$) in a volumetric ratio of 5 ml (0.5M): 2.5 ml (1M): 2.5 ml (29%): 5 ml (1M). The total reaction volume was adjusted with water to 43 ml. The temperature of the solution was kept at 27 °C +/- 1°C for 45, 60, 75 and 90 minutes respectively. The CuS films were cleaned in an ultrasonic bath with methanol followed by distilled water, rinsed and dried with $N_2$. The above described deposition process was repeated four times.

The optical properties were studied using a UV/VIS JENWAY 6850 UV/visible spectrophotometer. The morphology was studied in a SEM Zeiss SUPRA 40 with operating voltage of 5 kV. Raman Spectroscopy was carried out in a RAMAN - Microscope Themo Scientific DXR Raman. Chromium (Cr) contacts were deposited by sputtering in order to determine the electrical characteristics; (*I-V*) measurements at room temperature were performed in a Keithley 6517A semiconductor characterization system.

## 3. Results and discussions

The optical analysis of the CuS samples deposited over glass was performed using UV-Vis spectroscopy. This characterization technique is generally used for band gap determinations. UV-Vis spectroscopy was performed at room temperature in the range from 300 nm to 900 nm.

The UV-Vis spectra of the CuS films deposited on glass substrates are shown in Fig. 1. The optical transmittance spectra were obtained for the films deposited at different number of dips and different deposition times. The transmission in the visible region is in the range from 20 to 90 % depending on the number of dips and deposition time. The transmittance is low in the UV region for all the samples, which is similar or higher than the values reported in the literature [11-14]. Maximum transmittance is observed at wavelengths in the range from 500 nm to 700 nm. It is possibly due to a red shift in the films when the time or number of dips increases. The absorption measurement at various wavelengths (UV-Vis) of CuS films deposited on glass substrate was used to estimate the optical band gap. The Tauc method was used to obtain the optical band gap of the semiconductor compound (CuS thin films). Where, the relationship between absorption coefficient ($\alpha$) and the incident photon energy ($\alpha h\upsilon$) can be expressed as follows, $(\alpha h\upsilon)^2 = A(h\upsilon\text{-}Eg)$. The Eg is the optical band gap of the film and A is a constant [15]. The bulk band gap of CuS is 2.42 eV, as reported by earlier researchers [11-14].



a) b) c) d)

*Fig. 1. Absorbance spectra of CuS films deposited at different times and dips:*
*a) one, b) two , c) three , d) four dips.*

The obtained amorphous thin films exhibited a linear dependence of $(ahv)^2$ on $(hv)$ in the band gap range 2.60- 1.65 eV. As shown in each transmission spectrum the optical band gap value calculated from the amorphous thin films increased from 2.60 to 2.15 eV, from 2.25 to 1.95 eV, from 2.31 to 1.65 eV for increasing deposition time for one, two and three dips respectively; except for the amorphous film deposited with four dips. The reason for the nonlinear tendency in the band gap of films deposited with four dips may be the presence of structural defects [16]. In general the effect of gran size on the reduction of the optical band gap and red shift arises out of quantum confinement effects [17,18].

In order to compare films deposited with different number of dips, films deposited at 60 min were analyzed by SEM since those films exhibited a linear tendency for the calculated band gap; where the optical bang gap of the CuS thin films decreased from 2.35 to 1.8 eV as the of number of dips increased.

The grain size of the films was evaluated from SEM micrographs using the image processing Software ImageJ 1.37c. Fig. 2 shows images of the CuS films as function of the number of dips deposited at 60 minutes. It is clear that the grain size increases as the number of dips of the CuS increases.

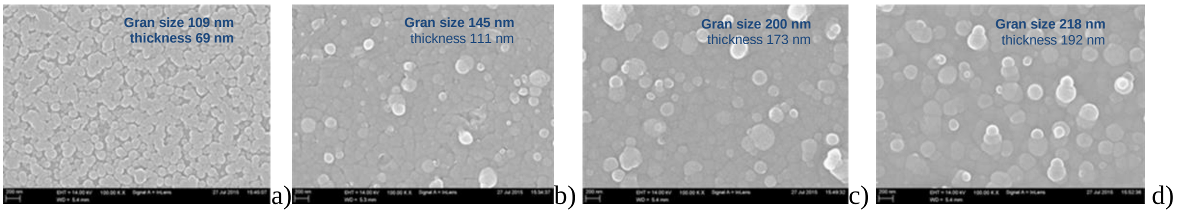


*Fig. 2. SEM for CuS films deposited with different number of dips and tim :*
*a) one, b) two, c) three, d) four dips at 60 min of total deposition time.*

The increased grain size is expected since additional CuS growth time leads to larger grains with the concomitant reduction in particle boundary density [19, 20]. It was observed that when the number of dips increases the grain size increases as well; nevertheless, in all samples, superficial grains are uniformly distributed. In addition, these grains tend to be rounded and increase their size with increasing number of dips. The average thickness of the CuS was obtained by measuring a step profile using AFM and also by cross-section imaging in SEM. The resulting thicknesses values are 69, 111, 173 and 192 nm for depositions from one, two, three and four dips respectively.

The Raman spectra of the CuS thin films, was used to analyze the composition of as-prepared CuS films deposited with different number of dips at 60 minutes, the resulting spectra is shown in Figure 3. The Raman spectra show one band at 475cm$^{-1}$ (Eg); which corresponds to the CuS vibration. The peak position is good agreement with previous Raman studies of CuS [21,23]. As can be observed the thickness increase due to an increase in the number of dips leads to a shift in the main peak. Moreover, according to the optical and microstructural characterization this effect can be associated to a change in the films microstructure.

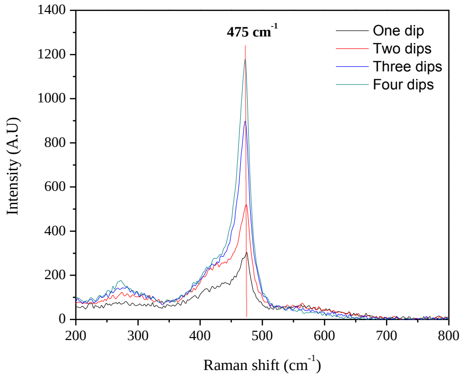


*Fig. 3. Raman Spectroscopy for CuS thin films deposited at 60 min with different number of dips.*

The dark electrical conductivity of the CuS films was measured with a two point probe approach at 300 K in air atmosphere. The change in the electrical conductivity (σ) of CuS thin films was analyzed as a function of the number of dips and grain size. I-V characteristics of the CuS thin films are shown in Fig. 4. It was observed that the remarkably larger forward current at all voltages has been obtained for CuS thin films deposited at two and three dips; the latter implies a higher conductivity in these films. This observation may be due to structural changes occurring in films with the abovementioned number of dips. As the number of dips increases, the structural properties improve leading to an increase in the average grain size as seen from the SEM characterization. The increased conductivity may be helpful in improving the semiconductor efficiency in applied devices.

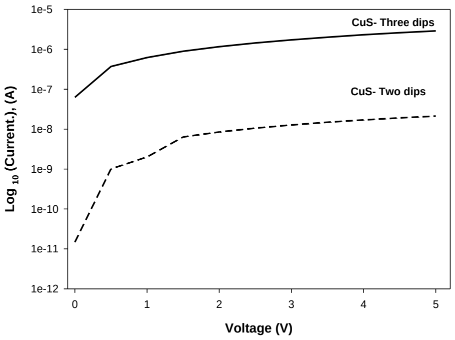


*Fig. 4. Current – voltage characteristics of CuS films.*

## 4. Conclusions

CuS films were successfully deposited at room temperature by the CBD method as function of different deposition time and number of dips. We have found a correlation between the physical properties and the CuS deposition protocol with a different number of dips and total deposition time. The microstructure, optical band gap and conductivity were found to be dependent on the deposition conditions. Films deposited with one, two and three number of dips showed a linear tendency on optical properties as observed by the change in the percentage of transmittance and optical band gap (2.60-1.65 eV depending on the deposition time and number of dips) up to 60 minutes of deposition time and three dips. However, films deposited at 75 minutes with four dips showed non-linear behavior in the optical properties, probably due to structural defects. The thin films deposited at 60 minutes with different number of dips were found to exhibit more uniform morphology, showing good ohmic behavior. The increase in the electrical conductivity with the increase in the number of dips is due to the increase in grain size influenced by the number of dips in the chemical bath. The characteristics obtained from different deposition time and number of dips makes these CuS films a suitable candidate for various semiconductor device applications, with the added advantage of being obtained through a rapid and low-cost technique; moreover, the work presented here can be extended to the study and deposition of other chalcogenide thin films of interest.

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