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# THE EFFECT OF COPPER DOPING ON SOME PHYSICAL PROPERTIES OF CHEMICAL SPRAYED CdS THIN FILMS

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**ABSTRACT**

Binary compound semiconductor of cadmium sulfide (CdS) and copper doped cadmium sulfide (CdS:Cu) thin films have been deposited onto glass substrates at substrate temperature ($T_s$=653 K) by chemical spray pyrolysis technique. Different doped films were prepared by using different volume concentrations of Cu in the spray solution (0.1-2%). The effect of copper doping on some physical properties of the prepared films of thickness (0.9 ± 0.05 µm) was investigated. The structural, optical and electrical properties of the thin films have been studied using X-ray diffraction, optical transmission spectra and electrical conductivity respectively. These properties were found to be strongly dependent on the doping concentration.

The polycrystalline films with a hexagonal structure for undoped and a mixed (hexagonal+cubic) structure for doped films have been obtained. The optical band gap energy of these films was found to be decreased from 2.451 to 2.410 eV with increase Cu concentration. The electrical conductivity of these films was found to be decreased initially with increasing Cu concentration, while it started to increase for doping values over 1% of Cu, and a conversion of the conductivity type of the films (from n-type to p-type) was observed at doping level above 1%.

**Keywords**: CdS thin films, Cu doping, spray pyrolysis, structure, optical and electrical properties.

## I. INTRODUCTION

Cadmium sulfide is an n-type semiconductor, it is one of the most studied compounds with a direct band gap of about 2.42 eV at 300 K that has been used extensively in many applications, including photo resistance sensors, low cost solar cells for energy conversion, light emitting diodes, laser materials, optical waveguides and nonlinear optical devices [1-3]. Several methods have been used to fabricate CdS thin films, among them the chemical spray pyrolysis technique is a simple and easily scalable method to prepare large area at low cost and uniform thin films, also it is a facile way to dope material by merely adding doping element to the spray solution [4-6].

The as-deposited CdS films has n-type conductivity [3], high dark resistivity ($10^5$ -$10^8$ Ω cm), to make the CdS films useful in optoelectronic applications, the dark resistivity must be reduced from to almost (10 Ω cm). Moreover, on this view preparation of p-type CdS thin films is need. Several ways were tried to reduce the dark resistance of the CdS films, such as the introduction of metal impurities in the deposition process or after the deposition of CdS films [7]. Such ways are expanded the application fields of CdS films. Moreover, the doping of copper changes the band gap energy of CdS and also improves its structure [8-10].

The aim of the present work is to study the effect of copper doping on structural, optical and electrical properties of the CdS thin films prepare by chemical spray pyrolysis technique.

## II. EXPERIMENTAL DETAILS

### II.1 Sample preparation

Cadmium sulfide (un-doped and copper doped) thin films were prepared by spray pyrolysis technique on glass substrates kept at 653 K. The samples were prepared by a technique similar to that described by (T.A. Abbas) [11], and the detailed description of the spray technique is given elsewhere. The precursor solution of CdS thin films was prepared by dissolving 0.1 mole of cadmium chloride with 0.1 mole of thiourea (which are suitable starting materials to produce satisfactory CdS films) [12] in double de-ionized water, then both components were mixed. For CdS:Cu thin film, a salt of $Cu(NO_3)_2$ with 0.1 mole solved in a double de-ionized water, then it was added to the mother solution with required percentage volumes. Each of the produced solutions and the mixtures ultrasonically agitated for (30 min) in order to obtain a good mixed solution.

It is necessary for the consistency of the film properties and for proper adhesion of the films that the surface of the substrate be absolutely clean and uncontaminated. The cleaning of glass substrates done by rinsing them with distilled water, then they were ultrasonically cleaned by immersing them in ethanol bath for 30 min, and then rinsed thoroughly in acetone. Finally, the substrates were dried by a stream of warm air.

The solution was atomized by a glass nozzle sprayer have a diameter of about (0.5 mm), by compressed nitrogen (as a carrier gas) with flow rate (8.5 L/min) and spray rate (15 ml/min).

The distance between the spray nozzle and the substrate is 30 cm with direction angle ~90°(which is a critical factor in order to obtaining a homogenous layer). The spraying period was (5 sec) which was followed by (55 sec) of waiting to avoid excessive cooling of the substrate. After the deposition has done, the samples were cooled down slowly to room temperature for (30 min), because slow cooling contributes perfect chemical reactions as well as complete re-crystallization.

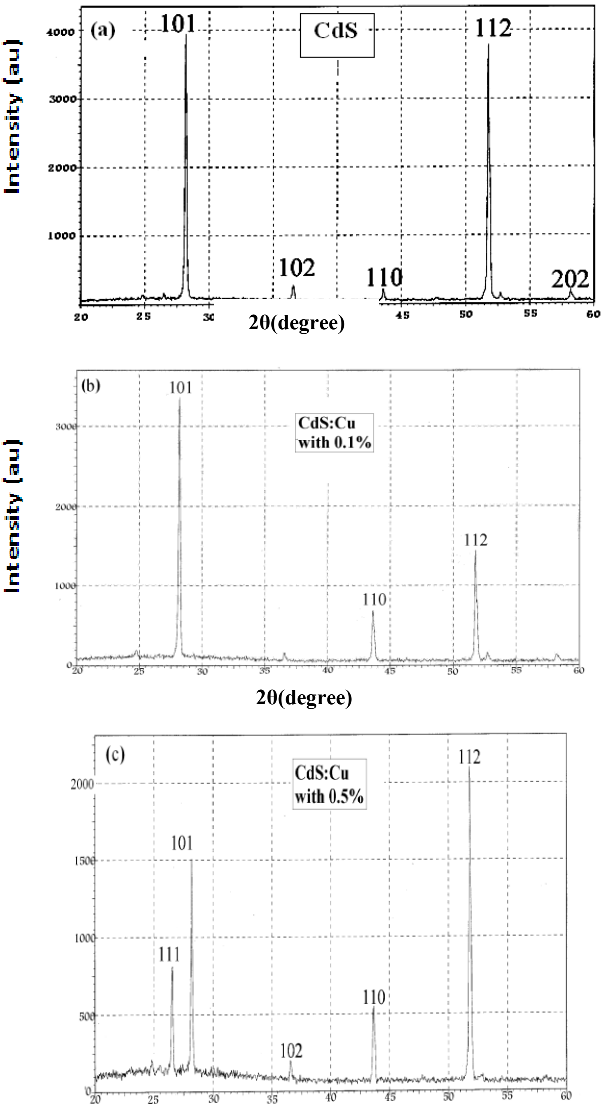
### II.2. Measurements

The struractural data of the films were obtained using X-ray diffractometer apparatus technique type (PANalytical X–Ray diffractometer with CuK$_\alpha$ radiation λ=1.5406A$^\circ$). The optical transmittance measurements spectra were carried out at room temperature using (Shimadzu UV-VIS mini 1240) spectrophotometer in the wavelength range (300-900 nm). The electrical conductivity measurements were taken at room temperature using two point probe method. Hot point probe measurements were also done to know the conductivity type of the films. Aluminum was chosen to make the ohmic contact by vacuum evaporation under the vacuum pressure of ($0.2\times10^{-5}$ torr).

## III. DATA ANALYSIS

### III.1 Structural properties

The X-ray diffraction spectra of all the prepared samples (CdS and CdS:Cu) are shown in fig.(1).



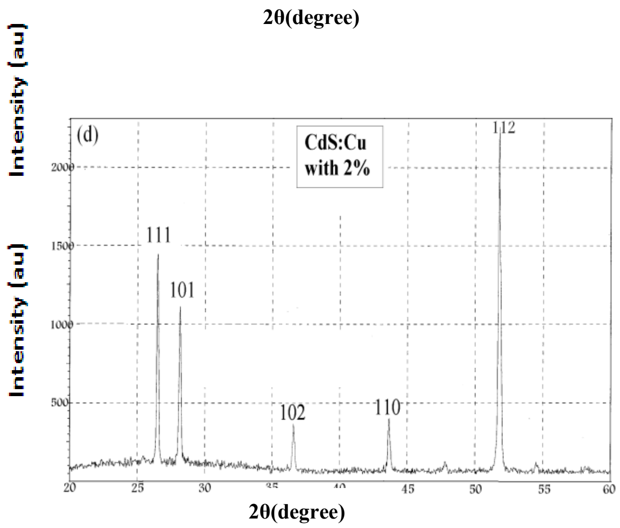




**Fig.(1):** XRD pattern of CdS & CdS:Cu thin films for different Cu concentrations.

The structural analyses of undoped CdS films in fig.(1-a), shows a strong XRD peak at the diffraction angle 2θ=28.21$^o$ corresponds to the (101) plane with secondary peaks (102) and (112) at 2θ=36.63$^o$, and 2θ=51.85$^o$, respectively. These identifications of the peaks indicate that the film has hexagonal structure in polycrystalline state with a preferred orientation of the (101) diffraction plane. This predominant peak is similar to that obtained by others [13,14].

The XRD pattern of Cu-doped CdS thin films with different concentrations, fig.(1-b,c and d), shows a hexagonal structure for low Cu concentration with a preferred orientation along the (101) plane and the weak orientation (110) had grown. Further increase in Cu concentration leads to appearance of a cubic structure with a preferred orientation along the (111) plane beside the hexagonal one. This is may be due to that Cu atoms with low concentrations take the place in CdS lattice as interstitial positions, but with higher concentrations, Cu atoms can form the precipitations of $Cu_2S$ cubic structure [15]. The grain size of the films was calculated by using Scherrer formula [16]:

$$D = \frac{0.94\lambda}{\beta\cos(\theta)} \qquad (1)$$

where λ is the wavelength of the X-ray used (1.54060 A°), $\beta$ is the full-width at half-maximum (FWHM) of the peak which has maximum intensity and $\theta$ is the Braggs angle.

It was found that the sharpness of the peak (101) decreases with increase in Cu concentration, and the (FWHM) of the peak increase, which in turn decreases the films grain size. The grain size was found to be 581.24 A$^o$ for the as deposited CdS and 576.33, 522.39, 504.75 A$^o$ for CdS:Cu (0.1, 0.5 and 2% Cu) respectively. This result is in a good agreement with that reported by other workers [9,17].

### III.2 Optical properties

Using the absorption data, the band gap energy was estimated from the formula [18]:

$$(\alpha h\nu) = A\,(h\nu - E_g)^n \qquad (2)$$

where ($h\nu$) is photon energy, $E_g$ the optical band gap of the film's material, A is constant and the value of n depends on the type of transition, where n=1/2 for direct band gap material.

By plotting $(\alpha h\nu)^2$ versus ($h\nu$) for all the samples, the energy band gap have been obtained, the linear nature of the plot indicates the direct band gap of CdS material. The intercept on the energy axis gives the value of the direct band gap, $E_g$ was 2.451 eV for the as deposited (pure) CdS films and 2.45, 2.43, 2.41eV for CdS:Cu (0.1, 0.5 and 2% Cu) respectively, as shown in fig.(2).

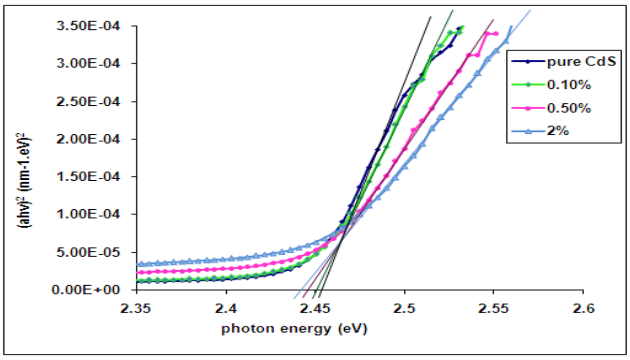



**Fig.(2):** Variation of [α(hν)]2 with photon energy for undoped and Cu doped CdS films with different concentrations.

It is clear that the energy band gap of the films was decreased with increasing Cu concentration. This is may be due to the structural modification of CdS thin films after the doping, or it may be due the formation of a new $Cu_2S$ phases in CdS films as mentioned in XRD analysis.

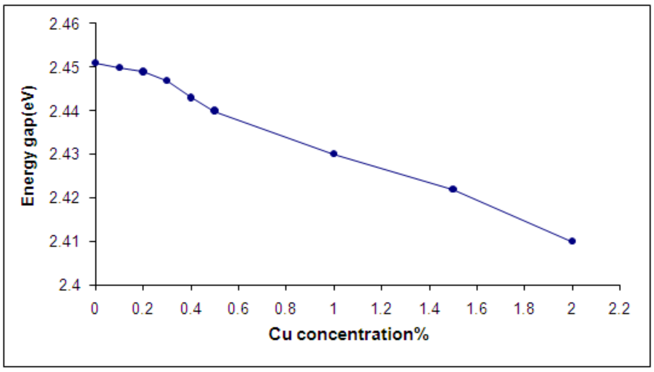



**Fig.(3):** Variation of the energy band gap of CdS films doped with different Cu concentrations.

Fig.(3) shows the variation of the obtained energy gap of CdS films with Cu doping concentration. The trend of the observed band gap variation after doping in the present study, is similar to that reported earlier [3,7,9,10].

### III.3 Electrical properties

The electrical conductivity (σ) of all samples have been determined using the formula[19] :

$$\sigma = \frac{L}{RA} \qquad (3)$$

where, R is the film resistance, L is the distance between the electrodes and A is the cross-sectional area of the films.

The room temperature electrical conductivity of as deposited CdS and Cu doped samples is shown in fig.(4).

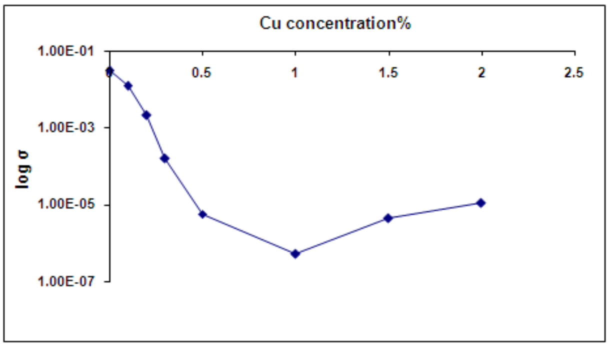



**Fig.(4):** The dark conductivity variation of CdS films with different Cu concentrations at room temperature.

It can be seen that the conductivity of the films decreased with increasing Cu concentration, until it reaches a minimum value at 0.1% Cu concentration, then it starts to increase with further increase of Cu. As it is known, the CdS thin films are usually grown as n-type conductivity due to native donors and sulfur vacancies [3,7], and that indicated by the hot point probe test. Copper is one of the more effective dopants to obtain a p-type CdS, because the vacance electron coming from $Cu^{+1}$ ions placed substitutionally in $Cd^{+2}$ sites, and copper ions produced in CdS lattice plays the role of an acceptor-type impurity [20,21]. The decrease of electrical conductivity at low concentration of Cu doping as indicated in fig.(4), is due to the compensation of donors by Cu accepters which are probably due to sulfur vacancies, the remarkable increase of electrical conductivity above 1% of Cu is due to the increase of Cu atoms substituted for Cd sites or due to formation of low resistive p-type copper-sulfur compound ($Cu_2S$) [22] and this gives rise to p-type conductivity in the films [23].

## IV. CONCLUSIONS

A study of structural, optical and electrical properties of undoped and copper doped cadmium sulfide thin films (CdS and CdS:Cu) prepared by chemical spray pyrolysis technique at a substrate temperature $T_s$=653 K, leads to the following conclusions:

1- The structural characterization done through XRD revealed that, the prepared films have a polycrystalline nature with a hexagonal structure for undoped and mixed (hexagonal+cubic) for doped films, and their particle size decreased with the increase in doping concentration of Cu.

2- The optical study of the films showed that the absorption spectra mechanism is direct transition. The band gap of the films decreases from 2.451 eV for CdS to 2.41 eV for CdS:Cu at 2% of Cu concentration.

3- The electrical measurements indicated that the conductivity of CdS films doped with copper was dependent on doping concentration. Low conductance CdS thin films can be prepared by using low concentration of Cu as a dopant. The conductivity of CdS thin films converted from n-type to p-type at doping level of Cu concentration above 1%.

4- As a final result of the doping study, it can be conclude that the modifications of CdS thin films properties were observed by copper doping process, and this is a very important result for solar cell applications.

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