P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2007,(1), (3) :70-79

THE EFFECT OF C u AND Sn ON SOME PHYSICAL PROPERTIES OF CdS THIN FILMS PREPARED BY SPRAY PYROLYSIS

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A R T I C L E I N F O

Received: 10 / 6 /2007
Accepted: 19 / 11 /2007
Available online: 14/6/2012
DOI:10.37652/juaps.2007.15604

Keywords:
CdS thin films,
spray pyrolysis,
Cu & Sn doping,
optical & electrical properties.

A B S T R A C T

In this investigation, thin films of CdS doped with Cu and Sn were prepared on glass substrate using spray pyrolysis techniques. The X-ray diffraction results obtained that the films are polycrystalline and having many phases depends on the doping type. The optical properties of the prepared films were studied in the range of wavelength (300-800)nm. The analysis of the absorption spectra of these films indicates that the films are of direct energy gape of values in the range (1.3-2.5)eV, depending on the type and concentration of the doping .The measurement of refractive index (n) and extinction coefficient (K) obtained that, they were having a changed values in the VIS region with doping concentration. The electrical properties of the prepared films were also studied, it is found that the films having a two activation energies. For 7mass%Sn E_{1act} equal 0.164eVat the temperature interval (295-325)K and E_{2act} equal 0.861 eV in the temperature range (325-425)K. Whereas at 25 mass%Sn,E_{1act} equal 0.108eVin the range (295-370)K and E_{2act} equal 0.542eV in the range (370-450)K. from Hall experiment found that all thin films which doped by Cu and Sn are given P-type.

Introduction

The production of п and VI related compounds by spray pyrolysis technique are convenient and inexpensive method for production large area solar cells [1-4]. The energy gap and the film composition depend on the spraying solution composition.

Thin film studies of CdS type materials are quit important because of their wide applications e.g displays systems and flat Tv .screen, sensitive photoconductor, IR detector, solar cell, etc.

Doping of optical materials has been subject of interest for many years, in order to modify their physical properties for varied applications .CdS were doped with Al ,Cu, Mn [4-8],which found that spray pyrolysis CdS films have been converted in to p-type by diffusion Cu

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atoms, also the addition of Cu causes a drastic decrease in the resistivity value. The crystalline structure of CdS:Er layer was cubic zinc bland for all the doped layers prepared, and found the energy band gap (Eg) firstly increased after word dimension becoming . For the electrical properties, logarithm of σ versus 1/kT curves indicate an effective doping CdS as a result of the Er introduction the lattice of the material.

$Zn_x Cd_{1-x}S$ thin films doped with Cu , Sn ,In, and F were studied [9-12].They found that the transition was improved by doping concentration of Sn ,and the resistivity decreases with increasing the doping concentration .

In the present study Cu and Sn doped CdS thin films were prepared by spray pyrolysis technique and some physical properties such as structure optical and electrical have been studied and discussed.

Experimental

CdS thin films doped with Cu and Sn were prepared using the chemical spray pyrolysis method. The films deposited on micro glass slides which were first cleaned with detergent water and then dipping in acetone. The solution were prepared from $CdCl_2$, thiourea, $CuCl_2$ and $SnCl_2$,with different molarities ,then mixed the amount of solution for each experiment by a magnetic stirrer .We used a nitrogen gas instead of air for spraying the solution on a square slide glass of temperature ranged from $350C^0$ to $450C^0$. The film thickness was measured by optical method (pezos fringes) . The structure of the films was examined by XRD. The UV-VIS spectrophotometers type Hitachi was used to measure the absorptance and transmittans and then from these measurements, the optical parameters were calculated .The D.C conductivity was measured by Keithly digital electrometer. Also we use Hall experiment to know the type and concentration of the charge carriers.

Results and discussion

1- Crystal structure properties

The structure of CdS thin films doped with Cu and Sn have been determined from X-ray diffraction analysis,which obtained that all thin films are polycrystalline. Fig.1 shows the X-ray diffraction patterns of the thin films,with different Sn concentrations from this figure, when the concentration of Cu is 1.6 mass % and Sn was absent in the CdS solution, there is peaks related to CdS and Cu_2S. The main peak of CdS must be at 2θ=26.7° [13], but because there is a Cu at the solution it is shifted to a lower θ as shown in fig.1.

When added Sn to the solution at 7 mass%, the height of the CdS peaks where decreased because some of the sulfur atoms inter in the new compound (Cu_2SnS_3) . If the amount of Sn was increased to 25 mass% and 30mass% the pattern shapes are almost the same as the first concentration.

2- 2- Optical properties of thin films

A- The Optical Energy Gap(Eg)

Results of optical energy band gap (Eg) for CdS thin films doped with Cu and Sn at varied doping concentrations are shown in fig. (2 and 3). The absorption (α) and the band gap (Eg) are related by the following relation for the direct band gap materials [11].

$\alpha = c(h\upsilon - Eg)^{1/2}/h\upsilon$ ……...(1).

Where Eg the optical band gap and c is a constant.

Thus as shown in fig.(2), the band gap of materials can be determined from extrapolation of the straight line section of the (αhυ)2 vs hυ. The materials of present study are of direct band gap nature. Fig.2 shows the variation of energy band gap for CdS thin films as a function of mass percentage of Cu doped it with constant Sn concentration at 25 mass%. It can be noticed that the energy band gap has values ranged from 2.2eV at absence Cu to 1.3eV at 3.3 mass% Cu. The energy band gap of CdS thin films reported as 2.4eV[9], so the value of Eg was decreased slightly with added Sn only to the solution as shown in fig.(2) Although it has been reported that Sn does not effect the values of Eg [10] .But when added Cu as well as Sn to the solution, Eg decreased continuously with increased Cu amount until it reached to 1.3 eV at 3.3 mass% of Cu, which agreement with somw authors, were they found that the Cu decreased Eg value for chalcagenide thin films [5,14]. This decrease in energy band was attributed to variation of stochiometry, or to the presence of unsaturated defects which increase the density of localized states in the band gap and consequently decrease the optical energy gap [15].

Fig.3 obtained the variation of Eg for CdS thin films as a function of the amount of Sn in the solution at constant Cu concentration for 1.6 mass%. From this figure, found that at absence Sn, the value of Eg decreased to 2eV due to added Cu amount to the solution. But when added Sn to the solution the value of Eg increased and then decreased depending on the concentration as shown in fig.3. The increased Eg with increased Sn concentration may due to the superposition of the absorption curves due to the presence of different phases in the films with different optical properties, which can shift the absorption characteristics [16].

B-The optical constants (n and k)

The values of refractive index (n) are calculated from the following relation [17] :

$$n= [\frac{4R}{(R-1)^2} - K^2]^{1/2} - \frac{R+1}{R-1} \qquad ....(2)$$

Where R is the optical reflectivity .

The values of n plotted vs λ as shown in figure (4) for CdS: Cu thin films with and without Sn. When Sn does not found in the solution, the graph shows a minimum values of n in the visible region of electromagnetic spectrum between (400-550 nm) and the value of n equal to 0.25. But, when the wavelength increased , n was increased also. If the value of Sn in the solution become 30mass %,the minimum values of n in the visible region are shifted to the range of (550-650 nm), so a red shifts of n value are happen , this means that there is anew crystal phase found. By relating to the XRD pattern fig.1, we show anew compound which is Cu_2SnS_3 in the amount of 30 mass%. The values of n in the regions before and after (500-650nm) are higher than others, and it have a value in the range (500-650) K of 1.3, this means that electromagnetic radiation is 1.3 times slower in this films than in free space [18].

The values of extinction coefficient (K) are calculating from the following relation[17]:

$$K=\alpha\lambda/4\pi \qquad ....(3)$$

Where α is the absorption coefficient and λ is the wavelength of the incident radiation. The values of K are plotted vs λ for different Sn concentration as shown in fig.5,. When Sn is absence from the solution, K have a maximum value of 0.85 in the wavelength 550 nm. But when added 0.7 mass% Sn for the solution, the maximum values of K shifted to the wavelength range 550-625 nm. That means the absorption range of thin films are increased because a new compound was appeared in the film, which is Cu_2SnS_3, while the maximum value of K was decreased to 0.62. If the concentration of Sn in the solution increased to 30 mass%, the maximum value of K continuous by shifting toward red spectrum to include a maximum value in the range of 500-700 nm which is 0.55.

3- Electrical properties of thin films

The d.c electrical resistance (R) of thin films were measured with the variation of temperature by Keithly digital electrometer and from ohms low found the resistivity (ρ) as the following relation :

$$\rho= RA/L \qquad ....(4)$$

And then the conductivity (σ) given by :

$$\sigma = 1/\rho \qquad ....(5)$$

Where A is the area of thin film and L is the distance between probes.

The activation Energy Eact was found from the following relation[19]:

$\sigma = \sigma_\circ \exp -E_{act}/kT$ ………(6)

where σ° is a constant, k is a Boltzmann constant ,T is the absolute temperature The conductivity was calculated at the range 295-455K.The activation energy (Eact) calculated from the slope of the curve between logσ vs 1/T as shown in fig(6). This figure shows the value of logσ with 1/T for CdS:Cu,Sn thin films with different values of Sn concentration. From this figure we show that all films has two activation energies. This means that σ depends on the temperature ($\sigma \alpha T^{3/2}$).

The two activation energies means there is two charge transfer mechanism, one of they at lower temperature which come from the hopping at the local states which near the mobility edge. Whereas the other at higher temperatures comes from charge transfer in a far distance of mobility edge. Also this activation energy may due to decreasing the state density at this temperature and this related to change the mechanism of conductivity.

The conductivity value σ1 of CdS:Cu,Sn thin films at 300K equal to 0.149eV for 7mass%Sn and the activation energy E_{1act} for the same concentration at temperature interval (295-325)K equal to 0.164eV, while σ2 at 425K for the some concentration equal 1.22eV and E_{2act} equal to 0.868eV at the temperature rage (325-425)K.whereas σ1 at 25mass%Sn equal to 0.9eV and σ2 equal to 7.38eV,wheras E_{1act} equal 0.108eV in the interval temperature(295-370) K and E_{2act} equal 0.542eV at the temperature range (370-450)K.From these values one can see that σ increased with temperature and with increasing Sn concentration, whereas E1act and E_{2act} decreased with increasing Sn concentration

The increasing of Sn doping decrease the activation energy may related to increase the doping states in the forbidden band gap with increasing the doping concentration. The behavior of these results have been found compatible to those reported earlier [3,19]. From Hall experiment it found that all thin films which doped by Cu &Sn are given P-type conduction.

Conclusion

In this study the crystal structure, optical and electrical properties of CdS: Cu, Sn thin films have been investigated. From XRD analysis it was found that all thin films are polycrystalline and having many phases. The optical band gap (Eg) was decreased with increasing Cu concentration from 2.2 eV at absent Cu to 1.3 eV at

3.3mass %Cu, whereas it increased with increasing Sn concentration from 2 eV at absent Sn to 2.5 eV at 15 mass% Sn. From the conductivity measurement it was found that the films have two activation energies, the value of it decreased with increased of Sn concentration from (0.164 and 0.861) eV for E_{1act} and E_{2act} respectively at 7 mass% Sn to 0.108 eV and 0.542 eV for E_{1act} and E_{2act} respectively at 25 mass% Sn . All thin films which doped by Cu & Sn are given P-type conduction. It can be concluded that spray pyrolysis technique can be used to deposit polycrystalline thin films with different values of energy band gap depends on doping type and concentration. Also by doping it can be decreased the activation energy of thin films and change its type of conductivity. So this study obtained that can be prepared a good properties thin films to used in opto-electronic applications.

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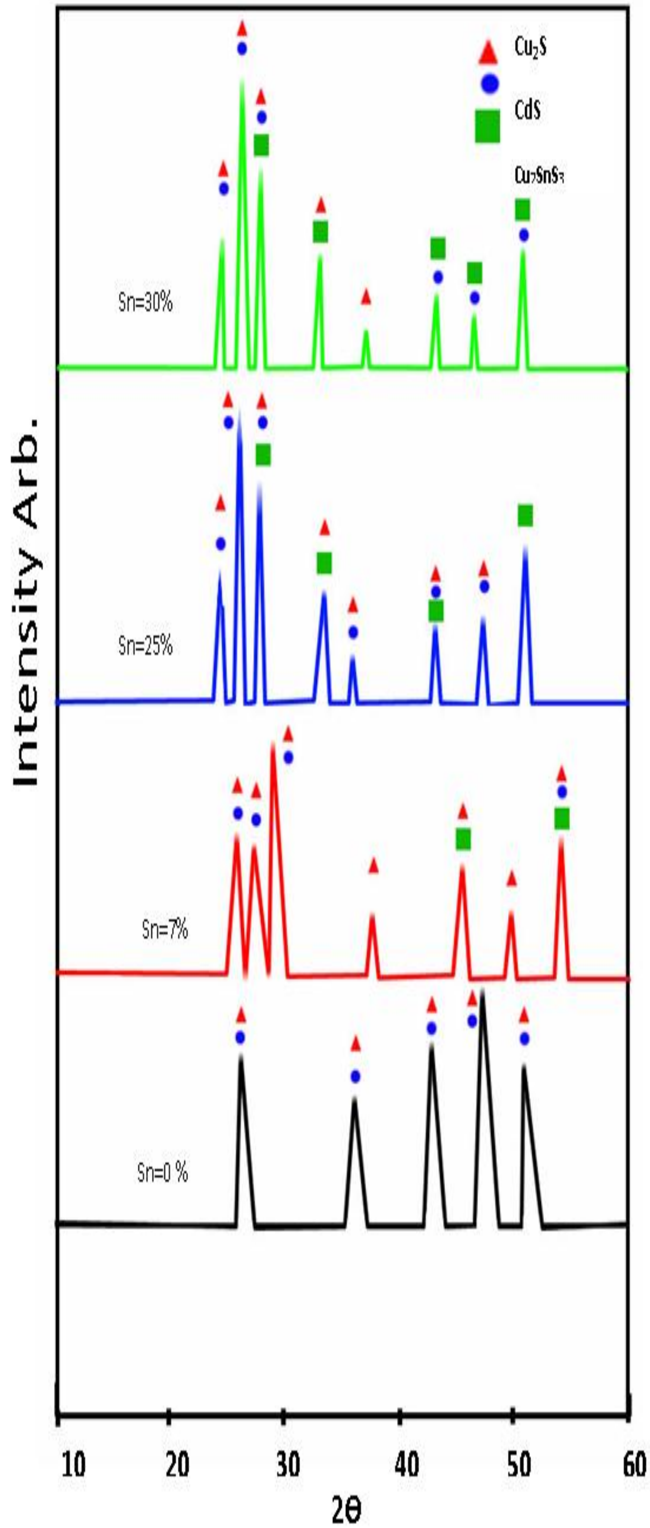

Fig.1 The XRD patterns of CdS : Cu, Sn thin films at 1.6 mass % Cu and different values of Sn .

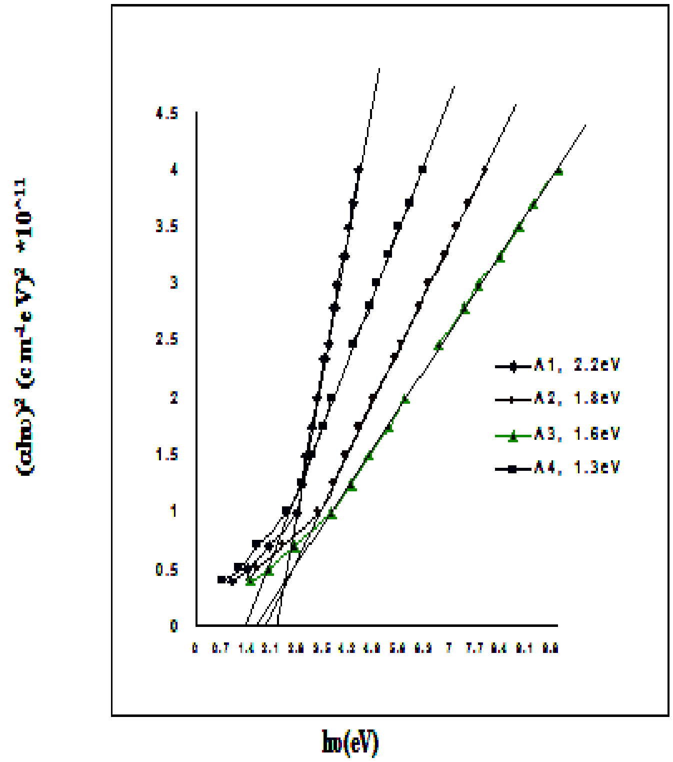

Fig.2 The variation of optical energy gap (Eg) of CdS : Cu , Sn thin films at 25 mass % Sn & different values of Cu , A1:0%, A2:1.3%, A3:1.6%, A4:3.3%.

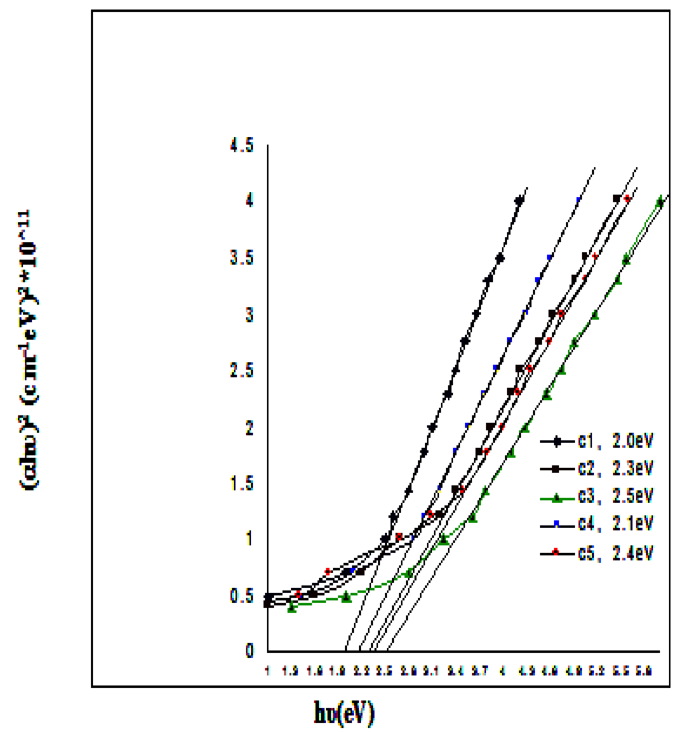

Fig.3 The variation of optical energy gap (Eg) of CdS : Cu , Sn thin films at 1.6 mass % Cu & different values of Sn , C1:0%, C2:7%, C3:15%, C4:25%, C5:30%.

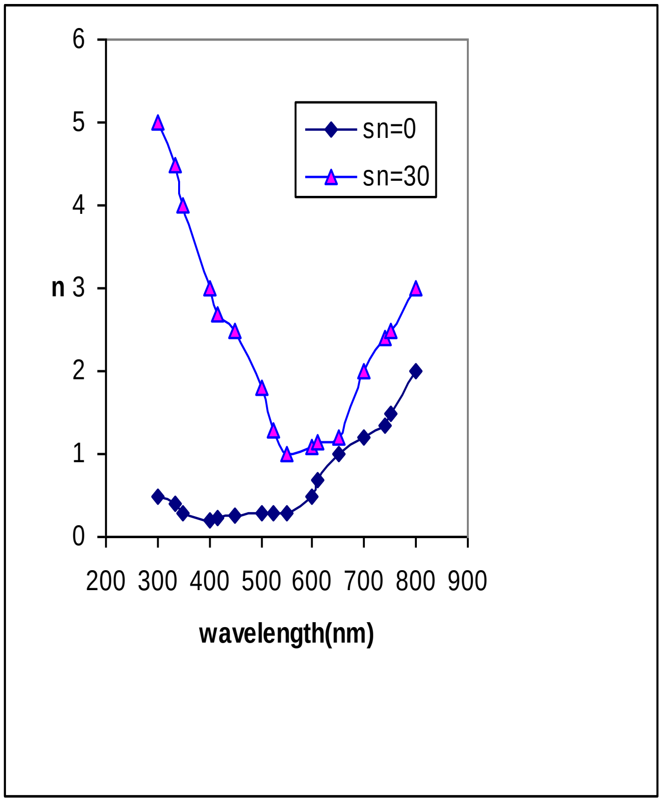

Fig.4: The refractive index (n) with wavelength (λ) of CdS : Cu,Sn thin films at 1.6 mass % Cu with and without Sn.

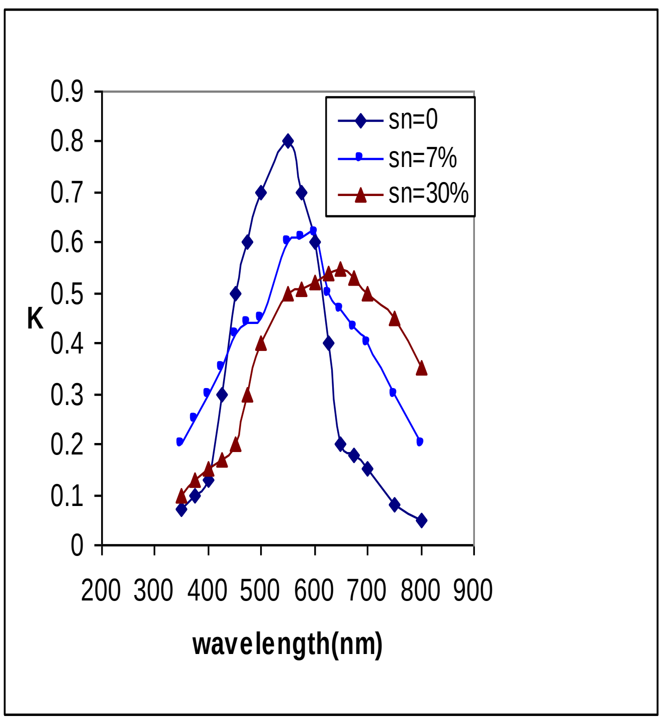

Fig. 5 : The variation of extinction coefficient (K) with wavelength (λ) of CdS: Cu,Sn thin films at 1.6 mass% Cu and different values of Sn .

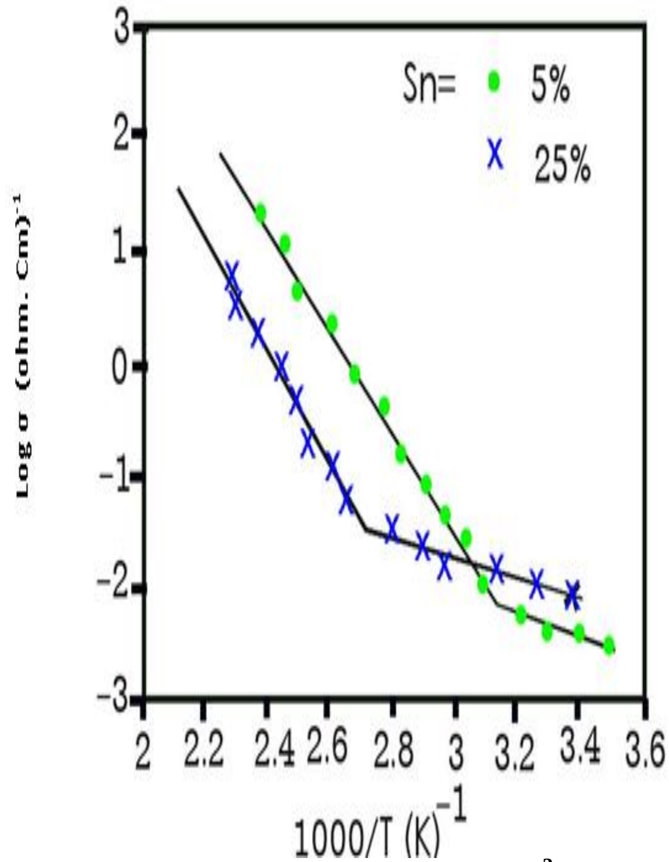

Fig.6 –The variation of log σ with 10^3 /T for CdS: Cu, Sn thin films at 1.6 mass % Cu and two different values of Sn.

P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
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تأثير النحاس والقصدير على بعض الخصائص الفيزيائيه للأغشية الرقيقة المحضرة بطريقة الرش الحراري CdS

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الخلاصة:

في هذه الدراسة تم تطعيم أغشية CdS الرقيقة بالنحاس والقصدير والتي حضرت على شرائح زجاجية بتقنية الرش الحراري .أظهرت نتائج حيود الاشعة السينيه بان الاغشيه متعددة التبلور وتمتلك عدة أطوار معتمدة على نوع التطعيم. تم دراسة الخصائص البصريه للاغشيه المحضرة في مدى الطول الموجي (300-800nm) ز ومن تحليل طيف الامتصاصيه لهذه الاغشيه تبين بانها ذات فجوة طاقه مباشرة وتمتلك قيم تقع بين (1.3-2.5eV) بالاعتماد على مادة التطعيم . قياسات معامل الانكسار ومعامل الخمود اظهرت بانهما يمتلكان قيم متغيرة ضمن منطقة الطيف المرئي مع تغير تركيز التطعيم. لقد تم دراسة الخصائص الكهربائيه للاغشية المحضرة واظهرت النتائج بأنها تمتلك طاقتي تنشيط . فعند التركيز 7mass%Sn فان E_{1act}=0.164eV في المدى الحراري (325-425K) بينما في تركيز 25mass%Sn فان E_{1act}=0.108eV في مدى (295-370K) وان E_{2act}=0.542eV في المدى الحراري (370-450K) . من قياس تجربة هول وجد ان جميع الاغشيه المطعمه بالنحاس والقصدير هي من نوع P-type .