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Structural, optical and electrical properties of doped copper ZnS thin films prepared by chemical spray pyrolysis technique

Mahdi Hasan Suhail* and Raoof Ali Ahmed**

**Department of Physics, College of Science, University of Baghdad, Jadiriya. Baghdad, Iraq*
***Directorate of Education Salahuddin, Education Department of Tuz, Iraq*

ABSTRACT

In this study, ZnSand Cu incorporated at (2%, 4%,6%, 8%, and 10%) thin films were growth onto hot glass substrates at substrates temperature 275^{0}C with thickness about 100$\pm$10 nm by chemical spray pyrolysis technique The spray solutions contains $Zn(CH_3COO)_2.2H_2O$, SC(NH2)2 and $CuCl_2.2H_2O$ with molar concentration 0.1M/L. The Structure of the prepared films were studied from XRD pattern, the results shows that the films were polycrystalline with cubic phase for pure ZnS and hexagonal phase for $Zn_{1-x}S:Cu_x$at x=10%.The optical properties of the films were studied using UV–VIS spectrophotometer in the range (350-1100) nm. The optical constants were studied as a function of the wavelength and increased with increasing Cu content for $Zn_{1-x}S:Cu_x$. The optical band gaps for the direct transition were estimate too and it was 3.44eVfor pure ZnS and increased with increasing Cu concentration from 3.50 to 3.69eV. Measurements of D.C conductivity with different temperature (298-473)K showed that D.C conductivity decreases while the thermal activation energy (E_a) increased with increasing Cu concentration.

Keywords: Thin film material, polycrystalline, optical constants, D.C conductivity, spray technique.

INTRODUCTION

ZnS compound is a white pellets has two crystalline structure which are wurtizte with hexagonal structure and zinc blend with cubic structure [1]. It was found that zinc blend changed to wurtizt phase at or before sublimation temperature, which affirm that the last phase is the most stable structure at high temperature [2]. Both wurtzite and zinc blend are intrinsic, wide band gap semiconductors .The hexagonal form of ZnS has a band gap of about 3.91 eV but the cubic form has a band gap of about 3.54 eV at 300 Kelvin[3]. ZnS can be doped as either an n-type or a p-type semiconductor.

ZnSis a potentially important to be used for application in a wide range of optoelectronic devices such as antireflection coating for heterojunction solar cells. It is an important device material for the detection, emission, and modulation of visible and ultraviolet light[4] . In particular, ZnS is believed to be one of the most promising materials for blue light emitting laser diodes[5].

The thin films of ZnS are usually prepared by different techniques such as sputtering, chemical bath , MOCVD techniques, vacuum evaporation , flash evaporation and spray pyrolysis [6-11].

Spray pyrolysis is a sample inexpensive method specially for substances which have water soluble salts. So we have used this method to obtain ZnS thin films on glass substrate.

The optical properties of the prepared film depend strongly on the manufacturing technique. The absorption of radiation that leads to electronic transitions between the valance bands (V.B) and conduction bands (C.B) and generates an electron–hole pair,these transitions are split into direct and indirect transitions and described by the equation[12]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^r \quad (1)$$

where A is constant which is proportion inversely with amorphousity, α is the absorption coefficient, $h\upsilon$ is the incident photon energy, and r is constant and takes the values (r= 1/2 and 3/2) for direct transitions allowed and forbidden respectively and (r=2 and 3) for indirect transitions allowed and forbidden respectively.The maximum wavelength (λ_c) of the incident photon which creates the electron–hole pair defined as [**8**]:

$$\lambda(\mu m) = \frac{hc}{Eg} = \frac{1.24}{Eg(ev)} \quad (2)$$

The intensity of the photon flux decreases exponentially with distance through the semiconductor according to the following equation [**9**]:

$$I_t = I_0 \exp(-\alpha t) \quad (3)$$

Where I_0, I are the incident and the transmitted photon intensity respectively. From equation (3) we can obtain absorption coefficient (α) where

$$\alpha = \frac{-2.303\, A}{t} \quad (4)$$

Where $A = \log I_o/I_t$ and represent absorbance.

The reflectance (R) has been found by using the relationship

$$R+T+A=1 \quad (5)$$

From normal reflectance, we have[13,14]:

$$R = (n-1)^2/(n+1)^2 \quad (6)$$

The optical constants such as extinction coefficient (k), refractive index (n), the real and imaginary parts of dielectric constant (ε_r, ε_i) respectively, were calculated by using these equations[15]:

$$K = \frac{\alpha\lambda}{4\pi} \quad (7)$$

$$n = (1+R^{1/2})/(1-R^{1/2}) \quad (8)$$

$$\varepsilon_r = n^2 - k^2 \quad (9)$$

$$\varepsilon_i = 2nk \quad (10)$$

Petritz and others[16] suggested model for the electrical conductivity of polycrystalline films when the conduction in the low temperature range take place through hopping because there is no sufficient energy to transport the charge carriers to another adjacent atoms ,thus the carrier hopes between the atoms located at the same energy ,in polycrystalline materials hopping take place at the grain boundaries .At high temperature the conduction occurs as a results of transporting of charge carriers thermally through the gains boundaries .

The D.C electrical conductivity of semiconductor (σ) is given by the formula:-$\sigma = q\ (n\mu_n + p\mu_p)$ (11)

Where μnand μpare the mobilities of electrons and holes respectively in units of (cm^2/V.sec),n and p) are the concentrations of electrons and holes and are measured in (cm^3) and (q) is the charge of electron.

The change of electrical conductivity with temperature of semiconductors is given by the equation [7]

$$\sigma = \sigma_0\, Exp(-E_a / k_B T) \quad (12)$$

Where Eais the thermal activation energy ,T is the absolute temperature ,kBis the Boltzmann constant and σ_0 is the minimum metallic conductivity (the value of σ when T→∞) . By taking (Ln) of the two sides of equation (12) we can get :

$$Ln\sigma = Ln\ \sigma_0 - E_a / K_B T \quad (13)$$

From determination of the slope we can find the activation energy

$$E_a = K_B\ .\ slope \quad (14)$$

MATERIALS AND METHODS

Pure and doped ZnS thin films were prepared on glass substrates (7.6x2.6x0.1)cm.The glass substrates were cleaned by distils water and alcohol respectively. Thespraying solution can be prepared by solving zinc acetate[$Zn(CH_3Coo)_2$(1.097g),thiourea [$CS(NH_2)_2$] (0.3805 g)&copper chloride [$CuCl_2.2H_2O$](0.852 g)in the distilled water to prepared solution with molarities (0.1) .The substrate temperature at 275± 10 ^{0}C was controlled using anNiCr- Nithermo-couple. The deposition time for one layer being about 2 sec. Thickness of the films was calculated by Optical Interference Fringes method. The thickness of all the prepared films were varied between 100-110 nm.

The structure of these films grown on glass substrates was examined by a Phillips X-raydiffractometer with CuK_α radiation of the wavelength (λ=1.541 Å) and radiation target in the range of 2θ between 20^0-60^0.

The optical transmission spectra of the deposited thin films were measured by UV-VIS spectrophotometer (model Sp-8001). The optical properties was calculated as a function wavelength in the range 350-1100nm.

The D.C. conductivity of the films deposited on the glass substrate with Al electrode could be calculated by using the electric circuit which is consists of oven type Memert, digital kethley to measure the resistance as function to temperature in the range (25-200)^{0}C. The activation energy of the pure and doped ZnS films can be deduced from the slope of the plot of ($Ln\sigma_{d.c}$) versus the reciprocal temperature in Kelvin (1000/T).

RESULTS AND DISCUSSION

3-1 structural properties

Figure (1) show the XRD patterns for pure ZnS and $Zn_{1-x}S:Cu_x$ thin films at x=6 and 10%. The XRD pattern shows apolycrystalline structure and have mixture of cubic phase for ZnS films and hexagonal phase for $Zn_{1-x}S:Cu_x$ according to American standard of tasting materials (ASTM) card[JCPDS-ICDD files No. 96-500-0089for cubic ZnS , No. 96-101-1197 for hexagonalZnS and No.96-900-0524 forCuS].

The grain size was calculated fromScherer's formula[17]:

$$D=\frac{0.9\,\lambda}{\beta\ cos\theta} \quad (15)$$

While the inter planners spacing (d) were calculated fromBragg's law[6] :

$$n\,\lambda = 2\,d\,\sin\theta \quad (16)$$

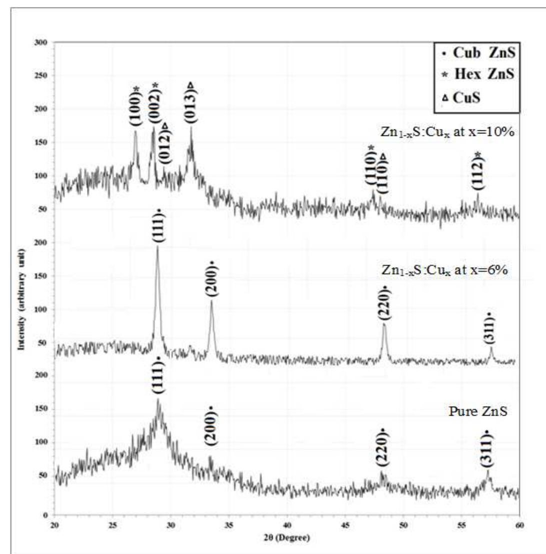

Fig. (1)XRD patterns for pure ZnS and $Zn_{1-x}S:Cu_x$films at (x=6%, 10%)with T_s=275°C

3-2 optical properties

3-2-1 The Transmission spectrum

The Transmission spectrum of prepared pure ZnS and $Zn_{1-x}S:Cu_x$ thin films at 275°C With different x content(2% ,4%, 6% , 8% , 10%) are shown in Fig. (2). The moderately high transmittance of films throughout the UV- VIS regions makes it a good material for optoelectronic devices.

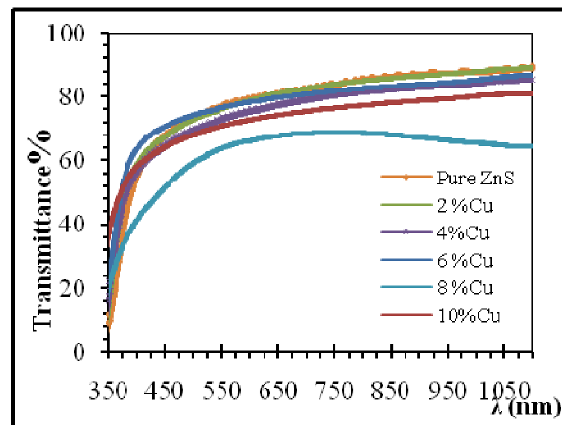

Fig. (2)The transmission spectrum for pure ZnS and $Zn_{1-x}S:Cu_x$films as a function of wavelength

3-2-2 Absorption coefficient

Fig. (3) shows the absorption coefficient as function of the wavelength for ZnS and $Zn_{1-x}S:Cu_x$. The calculated absorption coefficient for ZnS film was $3.2\times10^4 cm^{-1}$at λ= 600nm and a maximum absorption coefficient was for $Zn_{1-x}S:Cu_x$ film at x=8% [$4.1x10^4 cm^{-1}$] (see table 1).

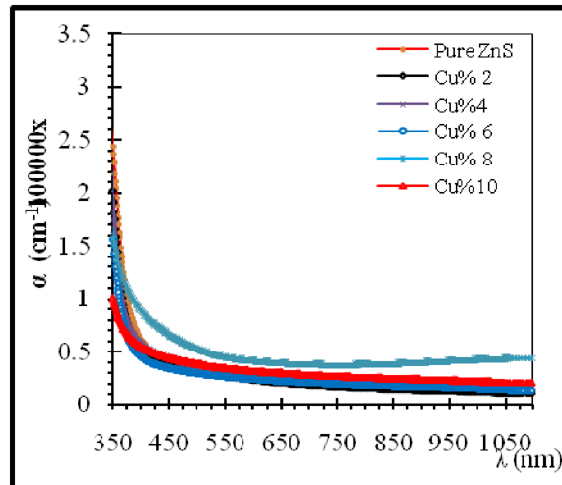

Fig. (3) The absorption coefficientfor pure ZnS and $Zn_{1-x}S:Cu_x$films as a function of wavelength

3-2-3 Extinction coefficient

Extinction coefficient (*k*)spectra versus wavelength as a function of different doping with copper is shown in Fig.(4). It can be noted that (k)increases highly at the absorption edge region corresponding to the increment in the photon's energy and the increase in the absorption coefficient with the decrease in the wavelength . In addition , it is clear from the figure that with the increase in the Cu concentration, in general the extinction coefficient (k)increases due to the increase in the depth of donor levels associated with sulfur vacancies .

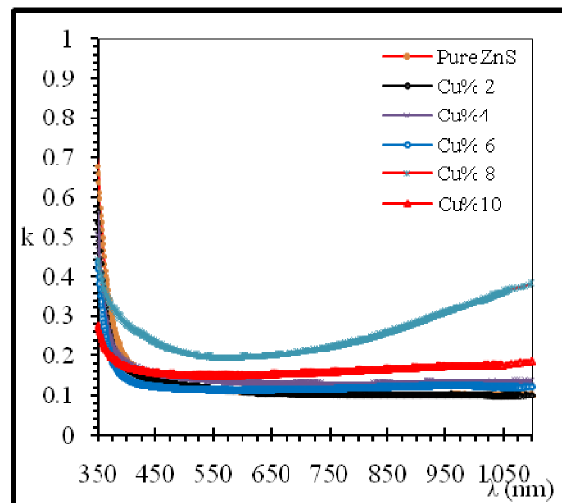

Fig.(4) The extinction coefficient for pure ZnS and $Zn_{1-x}S:Cu_x$ films as a function of wavelength

3-2-4 Refractive index

The variation of the refractive index as a function of the wavelength for Pure ZnS and $Zn_{1-x}S:Cu_x$thin films is illustrated in figure (5) . It is clear from this figure that the refractive index decreases with the increase in the wavelength of the incident photon . Also it can be observed , in general that the refractive index of the films increases with the increase in the Cu concentration.

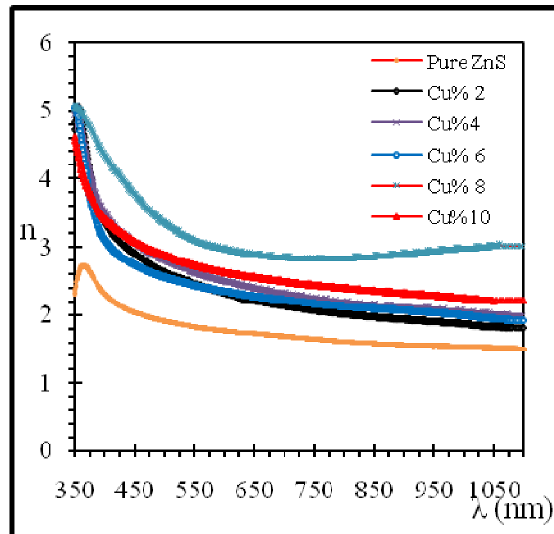

Fig.(5) Refractive indexfor pure ZnS and $Zn_{1-x}S:Cu_x$ films as a function of wavelength

3-2-5 The dielectric constants

Figure (6) and figure(7) illustrate the variation of the real part and imaginary of the dielectric constant as a function of the wavelength for Pure ZnS and $Zn_{1-x}S:Cu_x$thin films respectively. The real part of the dielectric constant (ε_r) depends mainly on the value of (n^2), because of the smaller values of (k^2) comparison with (n^2), whereas according to eq.(10) the imaginary part of the dielectric constant (ε_i) depends mainly on the (k) values which are related to the variations of the absorption coefficient.

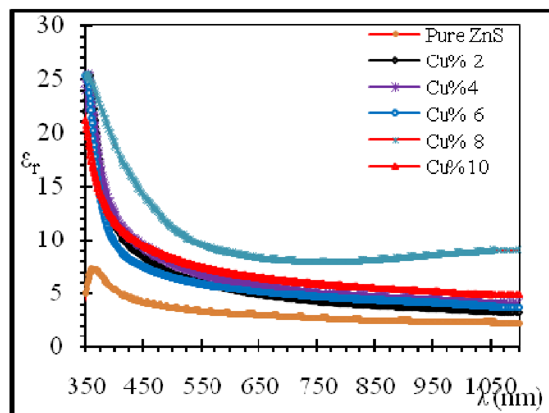

Fig.(6) The real part of dielectric constant for pure ZnS and $Zn_{1-x}S:Cu_x$ films as a function of wavelength

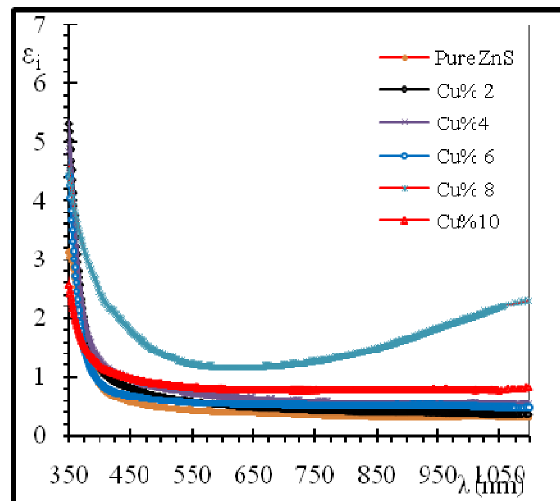

Fig.(7) The imaginary part of dielectric constant for pure ZnS and $Zn_{1-x}S:Cu_x$ films as a function of wavelength

3-2-6 The optical energy gap

The values of the band gap of ZnS thin film for the direct transition can be determined by extrapolating the straight line portion of the $(ahu)^2$against*hv,* as shown in Figure.(8). Direct band gap energy of ZnS thin films was estimated to be 3.44 eV, the value of the optical energy gap for direct allowed transition of ZnS thin films prepared at substrate temperature 275^0C is in good agreement with previously reported value saeed[9], andKrishnamurthiand Murugan[10]. The direct band gap energy of $Zn_{1-x}S:Cu_x$ thin films was increased with increasing Cu concentration from 3.50 to 3.69 eV (table1).

The wide direct band gap makes these films good material for potential applications in optoelectronic devices such as multilayer dielectric filters, and solar cell due to decreases the window absorption loses and that will improves the short circuit current of the cell.

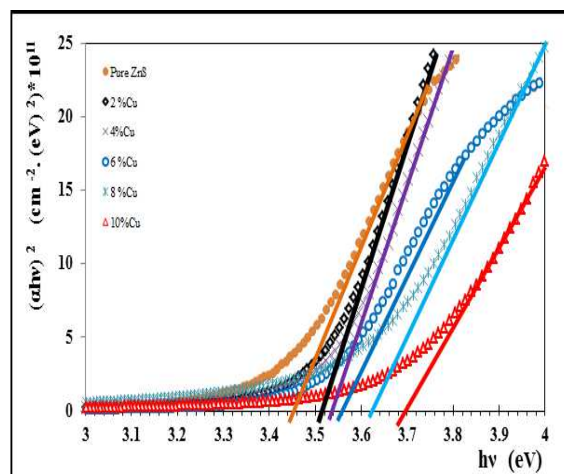

Fig.(8) The optical energy gap for pure ZnS and $Zn_{1-x}S:Cu_x$ films

Table(1): The Optical energy gap and the Optical constants Parameters for Pure ZnS and $Zn_{1-x}S:Cu_x$ Thin Films

$Zn_{1-x}S:Cu_x$						
X%	0	2	4	6	8	10
E_g^{op}(ev)	3.44	3.50	3.52	3.54	3.61	3.69
T% *at λ=600 nm*	79.21	78.90	75.49	78.45	66.31	72.88
α (cm^{-1}) *at λ=600 nm*	23306	23698	28120	24274	41086	31643
K *at λ=600 nm*	0.111	0.113	0.134	0.116	0.196	0.151
n *at λ=600 nm*	1.77	2.323	2.494	2.346	2.967	2.626
ε_r *at λ=600 nm*	3.117	5.384	6.202	5.489	8.763	6.875
ε_i *at λ=600 nm*	0.394	0.526	0.670	0.544	1.165	0.794

3-3 Electrical properties

Figure (9) shows the temperature dependence of D.C electrical conductivity ($\sigma_{d.c}$) for pure and doped ZnS films with different temperatures at range (298-473K).

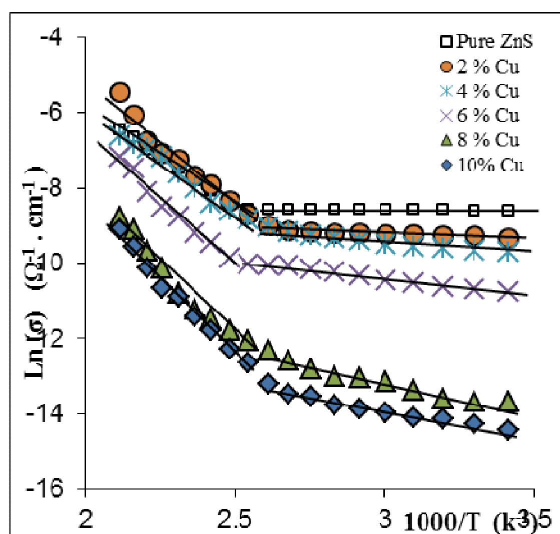

Fig.(9) The temperature dependence ($\sigma_{d.c}$) for pure and doped ZnS films at different temperature

There are two stages of conductivity throughout the heating temperature range .In this case the first activation energy(E_{a1}) occurs at low temperature within range(298-393) K and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands,while the second activation energy (E_{a2}) occurs at higher temperature within range (393-473) k and this activation energy is due to conduction of the carrier excited into the extended states beyond the mobility edge.These two conduction mechanism means that the D.C conductivity is non-linear with temperature. Table (2) shows the values of $E_{a1}$and $E_{a2}$and the values of D.C electrical conductivity ($\sigma_{d.c}$) , for all samples .It is found that ($\sigma_{d.c}$) decreased with increasing x content ,on the other hand the values of (E_{a1}, E_{a2}) declared to increase with increasing x content.

This is ascribed to the visual increasing in the band gap,the value of ($\sigma_{d.c}$) of ZnS films was($1.89x10^{-4}$) $(\Omega\text{-cm})^{-1}$at room temperature while ($\sigma_{d.c}$) value of $Zn_{1-x}S:Cu_x$ film with x=10% was ($5.43x10^{-7}$)$(\Omega\text{-cm})^{-1}$at room temperature,the difference in ($\sigma_{d.c}$) is due to the different degree of crystallinity of the prepared films.

Table (2) Values of E_{a1} and E_{a2} for pure and doped ZnS thin film at different Cu concentration

$Zn_{1-x}S:Cu_x$			
Cu%	E_{a1}(ev) at Range (298-393)k	E_{a2}(ev) at Range (393-473)k	$\sigma_{D.C} at\ R.T (\Omega cm)^{-1}$
0	0.003	0.395	1.81E-04
2	0.028	0.578	8.76E-05
4	0.067	0.459	6.14E-05
6	0.082	0.524	2.09E-05
8	0.147	0.634	1.13E-06
10	0.119	0.692	5.43E-07

CONCLUSION

pure ZnS and $Zn_{1-x}S:Cu_x$thin films weredeposited onto glass substrate by using spray pyrolysis technique, the films was successfully growth at substrates temperature of 275^OC.
XRD analysis shows that the deposited pure ZnS and $Zn_{1-x}S:Cu_x$ films are polycrystalline with cubic structure for pure ZnS and $Zn_{1-x}S:Cu_x$ at x=6% and hexagonal structure for $Zn_{1-x}S:Cu_x$ at x=10%.

Optical studies reveal that these films have a direct band gap and it is observed that the bad gaps increase with increase in the films x content, the transmittance is high in vis- NIR regions. The refractive indexes (n) and the extinction coefficients (k) are increases with increase in the films x content relative to pure ZnS film.

The DC-electrical measurement shows that the pure ZnS and $Zn_{1-x}S:Cu_x$ films have two stages of conductivity throughout the heating temperature range(298-473)K and that the values of E_{a1} and E_{a2}increase with increasing of x content for all films.

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