Iraqi Journal of Physics, 2008 *Vol. 5, No. 1, PP 63-70*

The effect of Cu concentration on some of the electrical properties of CdSe films

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Abstract

The CdSe pure films and doping with Cu (0.5, 1.5, 2.5, 4.0wt%) of thickness 0.9μm have been prepared by thermal evaporation technique on glass substrate. Annealing for all the prepared films have been achieved at 523K in vacuum to get good properties of the films. The effect of Cu concentration on some of the electrical properties such as D.C conductivity and Hall effect has been studied.

It has been found that the increase in Cu concentration caused increase in d.c conductivity for pure CdSe $3.75\times10^{-4}(\Omega.cm)^{-1}$ at room temperatures to maximum value of $0.769(\Omega.cm)^{-1}$ for 4wt%Cu.All films have shown two activation energies, where these value decreases with increasing doping ratio. The maximum value of activation energy was (0.319)eV for pure CdSe film in thermal range (293-363)K. Hall effect results has shown that the sample of pure CdSe film were n-type, while it is p-type for doping films. Also the charge carrier concentration decreases with increasing Cu concentration, and it varies between 2.1×10^{17} cm^{-3} for pure films, and $5\times10^{16}cm^{-3}$ for doping films with 4wt%Cu. The Hall mobility at laboratory temperature has been calculated, and it is increased exponentially from $0.012cm^2/V.sec$ for the pure film to 88.435 $cm^2/V.sec$ for doped films with 4wt%Cu. The drift velocity of these films increases with increasing doping concentration.

تأثير تركيز النحاس على بعض الخصائص الكهربائية لأغشية CdSe

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الخلاصة:

تم تحضير اغشية CdSe النقية والمطعمة بالنحاس (٠,٥ و ١,٥ و ٢,٥ و ٤ %) بسمك 0.9μm بتقنية التبخير الحراري على ارضية زجاجية وتم تلدين النماذج المحضرة عند درجة523K تحت الفراغ للحصول على اغشية ذات صفات جيدة ، كما ونم دراسة تأثير تركيز النحاس على بعض الخصائص الكهربائية كالتوصيلية المستمرة وتأثير هول.

اوضحت النتائج ان زيادة تركيز النحاس يؤدي الى زيادة في التوصيلية المستمرة عند درجة حرارة الغرفة للغشاء CdSe $3.75X10^{-4}(\Omega.cm)^{-1}$ وتصل الى قيمتها العضمى $0.769(\Omega.cm)^{-1}$ للأغشية المطعمة بتركيز ٤% نحاس. تبين ان جميع الأغشية تمتلك طاقتين للتنشيط وتنخفض قيمتها عند زيادة نسبة التطعيم وكانت قيمة طاقة التنشيط (0.319)eV لغشاء CdSe النقي عند مدى من درجات الحرارة (293-363)K

أوضحت نتائج تأثير هول ان اغشية CdSe النقية ذات نوع سالب بينما الأغشية المطعمة تكون ذات نوع موجب وكذلك ان تركيز حاملات الشحنة يقل مع زيادة نسب التطعيم ويتغير حيث كان للأغشية النقية 2.1×10^{17} cm^{-3} و 5×10^{16} cm^{-3} للأغشية المطعمة بتركيز ٤% نحاس. تم حساب تحركية هول عند درجة حرارة الغرفة حيث تزداد اسيا من $0.012 cm^2/V.sec$ للغشاء النقي الى $88.435\ cm^2/V.sec$ للأغشية المطعمة بتركيز ٤% نحاس.

□

Introduction

There are many applications in photoconductive, photovoltaic cells, and solid state devices for cadmium selenide which belong to II-VI compounds semiconductors. The performance of high quality CdSe thin film devices seems to depend on the preparation condition and other related treatmentsb [1,2]. Various methods have been reported for CdSe thin film preparation such as vacuum evaporation, chemical spray method and more recently by reaction of mixture containing Cd and Se solvents in the presence of reducing solution [3]. II-VI compounds semiconductors thin film give photoconductivity only if it is doped and crystalline, and the electrical properties of these films depend mainly on the impurity concentration and sensitization of the films [1]. Extensive studies have been carried out on the photoconductive properties of copper doped CdSe thin film[4]and were found that the conductivity was increased with increase of Cu impurity concentra-tion. The electrical properties measurements of semiconductor thin films allow determination of the impurity levels present in the materials and the parameters that are critical to their utilization in various electronic and optoelectronic applications. The electrical properties depend upon the nature of semiconductor if they are pure or doped, crystalline or amorphous [5]. Electrical conductivity (σ) is defined as the proportional factor between the current density and the electric field, and it's given by the equation[5]:

$$J=\sigma E \qquad (1)$$

Where J is the current density, E is the electric field. In semiconductors the relation between the current density and electric field is given by [6]:

$$J=q(n\mu_e+p\mu_h)E \qquad (2)$$

Where n & P are the electron and hole concentration and μ_e and μ_h are the mobility of electron and hole respectivily.

Then the relation between the conductivity and electron - hole concentration is:

$$\sigma=q(n\mu_e+p\mu_h) \qquad (3)$$

For most cases of semiconductor the following equation gives the change of the electrical conductivity with temperature [7]:

$$\sigma= \sigma_o \exp(-E_a/k_B T) \qquad (4)$$

Where (σ_o) is the minimum electrical conductivity at (0)K, k_B is the Boltzman constant, E_a is the activation energy which is corresponding to the ($E_g/2$) for intrinsic conduction or corresponds to the distance between the donor level and the conduction band edge for n-type extrinsic conduction, or corresponds to the distance between the acceptor level and the valence band edge for p-type extrinsic conduction, E_g is the energy gap[7].

When a current-carrying conductor is placed in a transverse magnetic field, the Lorentz force on moving charge pushes them toward one side of the conductor producing a charge separation and as a result, a voltage arises in the direction perpendicular to both the magnetic field and the current and called Hall voltage[8],as shown in Fig. (1). This is known as the Hall effect and it's widely used to distinguish between the type of the carriers, the concentration and to determine the carrier mobility in the semiconductor.

The Hall coefficient (R_H) is found by

$$R_H=\pm 1/nq \qquad (5)$$

If V_H is the Hall voltage across the slab, I is the current and B is the applied magnetic field, then the Hall coefficient is

$$R_H=tV_H/IB \qquad (6)$$

Where t is the thickness of the sample. If the conduction is due to the one carrier type (e.g: electrons) then we can find the mobility from the equation[8]:

$$\mu=\sigma\ /nq \qquad (7)$$

$$\text{and } \mu=\sigma\,(R_H) \qquad (8)$$

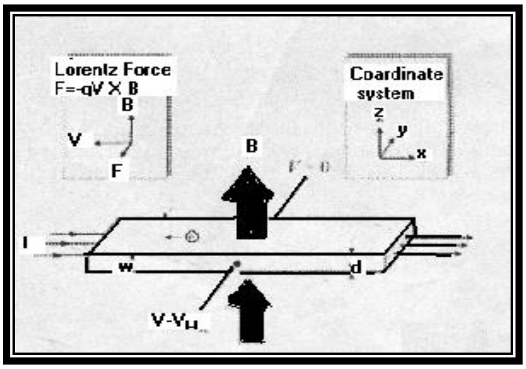


Fig (1) Schematic diagram of Hall effect [8]

The purpose of this work is to study for the first time the effect of doping Cu on some the electrical properties of CdSe:Cu such as conductivity, activation energy, carrier concentration, Hall mobility, and the drift velocity.

Experimental

Pure cadmium selenide (CdSe) pure was doped with copper by chemical diffusion by mixing it with solution of CuCl(0.5,1.5,2.5,4.0wt%) and dried at 373K for (2hours). CdSe:Cu films were prepared on glass substrate by vacuum evaporation with thickness (≈1)μm which measure by weighting method. The electrical resistance has been measured as a function of the temperature(T) using the circuit diagram shown in Fig.(2a). The measurements have been done with used sensitive electrometer type of (Keithly Digital Electrometer (616)) and vacuum electric oven. The resistivity and conductivity as a function of T and the activation energy can be calculated from these measurements by using eqs.(1&4). By plots the (Lnσ) vs. reciprocal of the absolute temperature ($10^3/T$), we can measure the activation energy according to equation(4).by taking the slope of straight lines which represent ($-\Delta E/K$) and multiplying it by Boltzman constant.

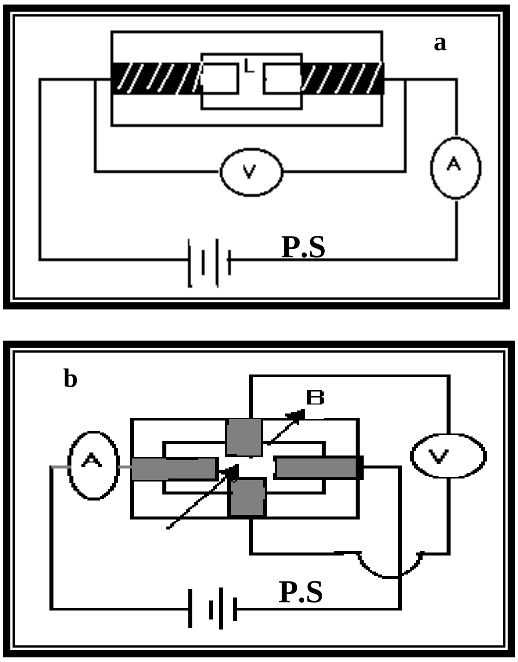


Fig-(2) The circuits used for measuring a-D.C conductivity b- Hall effect

Hall effect has been measured by using the electrical circuit shown in Fig. (2b), which contain (D.C power supply (0-40)V, then when the samples carrying a current expose an constant magnetic field (B=0.254)Tesla perpendicular to the electric field then an e.m.f which is called Hall voltage(V_H) is set up across the sample, then the I and V_H were recording by using Keithly Digital Electrometer616. The type, concentration and mobility of the carrier for CdSe pure and doped films with thickness (1)μm at different Cu concentration can be calculated by using eqs.(5-7).

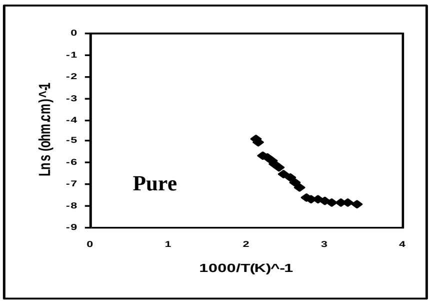
Results and Discussion:

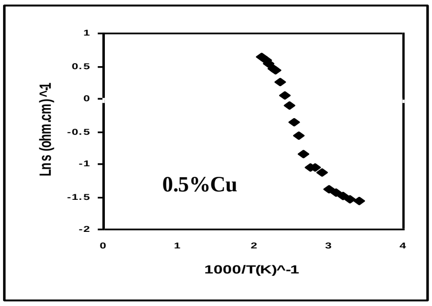
1-D.C Conductivity:

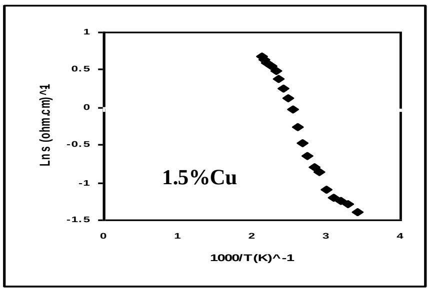
The variation of conductivity with temperature is the main tool in investigating the properties of semiconductors. It is very useful to determine in the extrinsic range the activation energies of impurity centers and in the intrinsic range the main energy gap. The d.c conductivity for CdSe pure and doping films has been studied as a function of (10^3/T) within the range (298-473)K as shown in Fig.(3)

It may be seen that the conductivity at room temperatures (R.T) increases approximately from $3.8\times10^{-4}(\Omega.\text{cm})^{-1}$ for pure CdSe , to $0.2079(\Omega.\text{cm})^{-1}$ for 0.5wt%Cu and then increases with increasing Cu concentration and arrive to maximum value $0.769(\Omega.\text{cm})^{-1}$, at 4.0wt%Cu as shown in Fig.(4), and theoretically this attributed to improve the crystal structure with increasing Cu concentration and decreasing the crystal defect and state density , and this nearly agree with Tallin [10], who found that the conductivity for CdSe increases with increasing Cu concentration.

We found that 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 (293-363)°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 (363-473)°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, also the variation of the defect and unstable Fermi level under variation of temperatures leading to varying the value of activation energies at this range of temperatures, therefore, we are observed two activation energies at this range of temperatures as in Fig.(3).







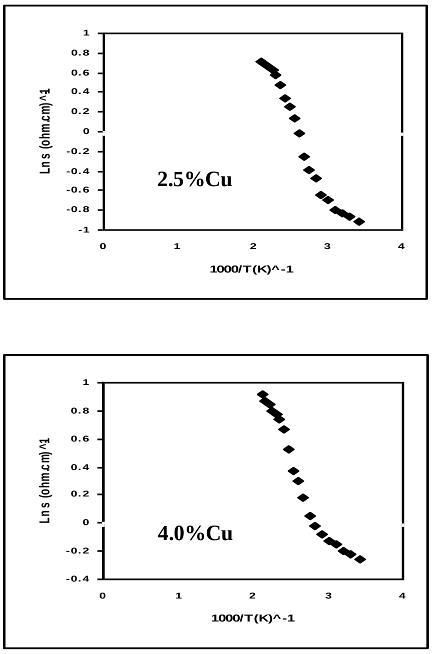


Fig.(3) The variation of ln σ as a function of (1000/T)

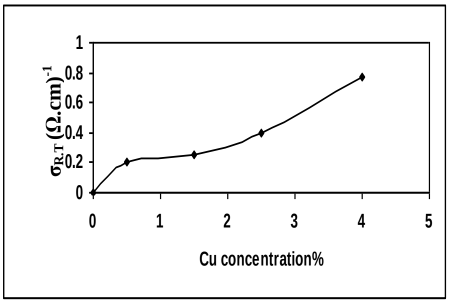
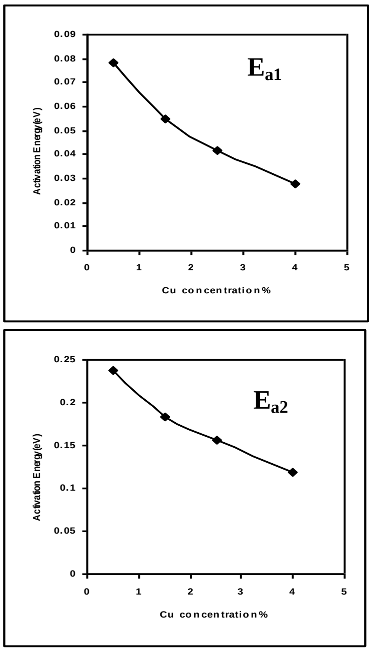


Fig.(4) The variation of conductivity as a function of Cu concentration

The value of activation energy for CdSe is small compared with energy gap for this material and this referring to localized states in the energy gap which caused by the structure defects, therefore the first activation energyE_{a1} was referred to hopping processes through the localized states near the mobility edge, and it is occur with helping of the phonons caused by vibration lattice, and the carriers transport from one localized states to the other, while the second activation energy (E_{a2}) occurs at higher temperature within range (363-473)K represents the transform beyond the mobility edge inside E_g, this mean decreasing of state density at this range of temperatures. We can see from Fig.(5a&b)that the value of activation energies decreases with increasing Cu concentration and this leading to deviation of Fermi level towards valence band due to increasing of doping level inside E_g, the value of E_{a1} decrease from 0.319eV for pure films to 0.028eV for doped films, while E_{a2} increased from 0.035eV to 0.237eV for 0.5wt% and then decreased with increasing Cu concentration and this may be due to change in the localized states, structure, and composition of the films as well as to the re arrangement of atoms which yields fewer defects, this mean that adding Cu will improved the structure and made on it dramatic change because that the researchers prove that the behavior of Cu was unknown and it is re- arrangement the structure of the films when doped with it [1,9]. Also we can see that that the maximum activation energy for CdSe:Cu occurs at 0.5wt% with value of 0.078eV, and the minimum activation energy occurs at 4 wt % with value of 0.028eV we can see from Table(1) that the (E_{a1})is smaller than (E_{a2})and this due to that the thermal impurity ionization at acceptor levels needed to minimum energy for transform the carrier.



Fig(5)The Variation of E_{a1} and E_{a2} as function of Cu concentration.

Also Shreekanthan *et al* [11] has studied the variation of resistance with temperatures for CdSe and they found that there are two regions at low temperatures region(293-330)K with thermal activation energy 0.34eV and a high temperatures region(330-520)K with thermal activation energy 0.186eV, and they attributed theses regions to the presence of donor states produced by excess cadmium and an intrinsic region setting in at a temperatures of 330K, this value of activation energy are agreement with our results.

Table(1)The parameters of d.c conductivity

Cu W_t%	$\sigma_{R.T}$ $(\Omega.cm)^{-1}$x10^{-2}	E_{a1} eV	Temp .range(K)	E_{a2} eV	Temp .range(K)
0	**0.00038**	**0.319**	**293-363**	**0.035**	**363-473**
0.5	**0.20790**	**0.078**	**293-363**	**0.237**	**363-473**
1.5	**0.25000**	**0.055**	**293-333**	**0.184**	**333-473**
2.5	**0.40000**	**0.042**	**293-333**	**0.157**	**333-473**
4	**0.76900**	**0.028**	**293-333**	**0.118**	**333-473**

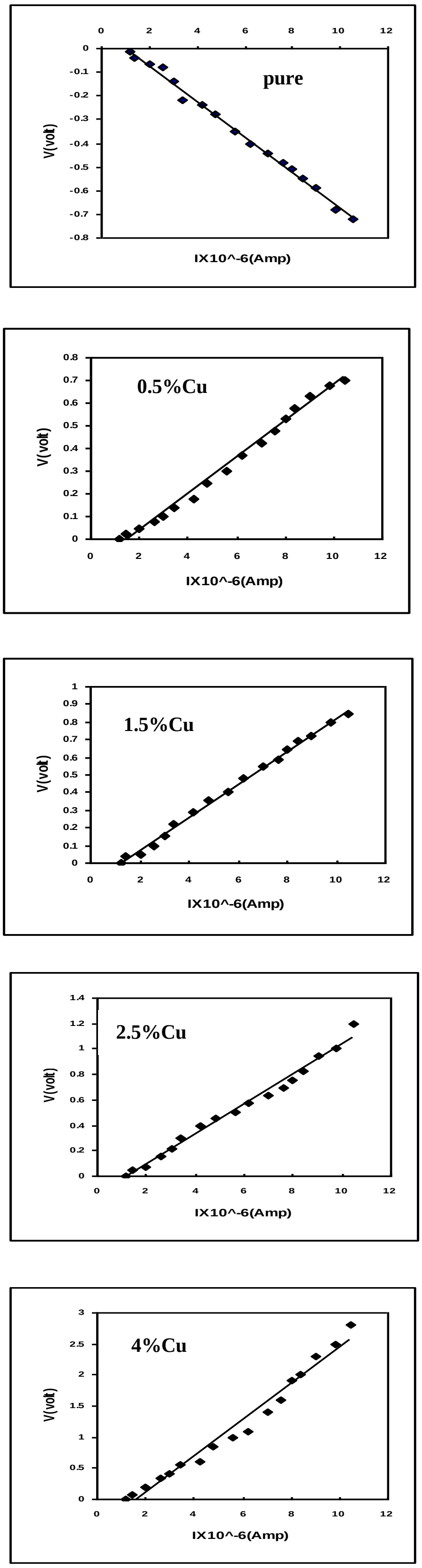
Study of Hall measurements

The variation of Hall voltage as a function of currents for pure CdSe and doping with copper at the concentration (0.5,1.5,2.5,4wt%Cu) has been studied as shown in Fig.(6). These measurements show that the pure CdSe films are n-type due to the presence of excess cadmium which may produce vacant in CdSe sites that form shallow donor levels and will not leave any un reacted sulfur inside the grains during the deposition and annealing films and this results agreement with other researchers Shreekanthan *et al*[11], Barua[12], and Snejdar *et al*[13]. While for CdSe:Cu films with Cu concentration (0.5,1.5,2.5,4wt%Cu) the R_H convert to the positive for films and that represent p-type conduction, this is attributed to the existence of Cu concentration which act as acceptor impurity as substitute site for cadmium and this agree with Tallin[10], Ture and Claybourn[14], and Ermolovich and Paveletes[15] as they found that Cu atoms as acceptor impurity in CdSe film. From Fig.(7) and Table(2), the value of carrier concentration decreases with increasing Cu from $2.1\times10^{17}cm^{-3}$ for CdSe films to $5\times10^{16}cm^{-3}$ for doped film with 4wt% Cu respectively as shown in Fig.(7a) and this is attributed to the re-crystallization films by adding Cu and fill all dangling bonds and decreasing the defect and density of states as we see in d.c measurements, also the Cu atoms act as acceptor impurity and the electrons transform from valence band to acceptor levels which mean that the conduction was made by holes. The value of carrier concentration which found by Sathyalatha et al[16], and Levey *et al* [17] was about $2.14\times 10^{17}cm^{-3}$, $6\times10^{17}cm^{-3}$ respectively, and this value are nearly agreement with our value.

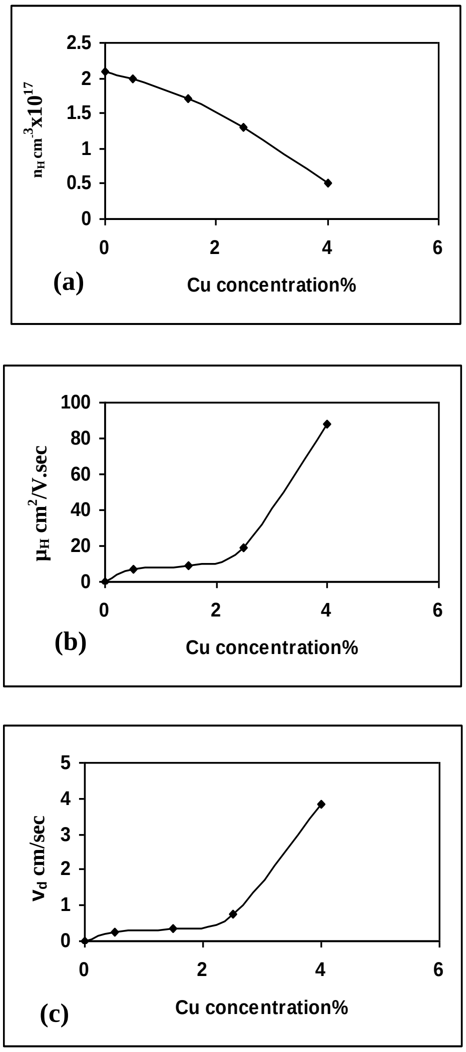
It is found that the mobility increases exponentially with increasing Cu concentration and this is attributed to reduction of the scattering of the carrier from the surface as well as due to the elimination of the defects in the films and increase in crystalline which due to decrease the number of grain boundaries as shown in Fig.(7b).Our value of mobility for pure CdSe and doping films was higher than the value of other researcher[12-15], also the drift velocity increases with increasing Cu content which is due to increase the mobility [seeTable(2) and Fig.(7c)].

Table(2)The parameters of Hall measurements

Cu W_t %	$\sigma_{R.T}$ $(\Omega.cm)^{-1}$x10^{-2}	R_H cm^3/C	n_H cm^{-3}x10^{17}	μ_H $cm^2/V.sec$	v_d cm/sec	type
0	**0.00038**	**29.72**	**2.1**	**0.012**	**0.0004**	**n**
0.5	**0.20790**	**31.4**	**2.0**	**6.520**	**0.2500**	**P**
1.5	**0.25000**	**36.7**	**1.7**	**9.175**	**0.3670**	**P**
2.5	**0.40000**	**46.4**	**1.3**	**18.560**	**0.7690**	**P**
4	**0.76900**	**115**	**0.5**	**88.435**	**3.8450**	**P**



Fig(6)The variation of Hall voltage as function of current for CdSe films



Fig(7)The variation of n_H, μ_H and V_d as function of current for CdSe films

Conclusions

1- The conductivity at room temperatures increases with increasing Cu concentration.

2- All films have been shown two activation energy, and these value decreases with increasing Cu.

3- The pure CdSe films was n-type, while the doped films were p-type.

4- The charge carrier concentration decreases with increasing Cu concentration.

5- The Hall mobility and drift velocity for prepared films increases exponentially with increasing Cu concentration.

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