

## Optoelectronic Properties of the Semiconductor Compound $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$

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### ABSTRACT

The electrical measurements were carried out under vacuum ( $10^{-1}$  torr) on different samples of the quaternary semiconductor compound prepared by slow cooling technique. Such measurements were also carried out on the thin films of the compound prepared by evaporation under vacuum and D.C. sputtering methods. The electrical conductivity and activation energies of the prepared samples were studied under the influence of annealing processes. Hall measurements indicating that the thin films are P-type. Mobility and concentration of the carriers were calculated at room temperature. The optoelectronic properties of the compound (single crystal, bulk and thin films) were also studied. The tail width of the localized states of thin films were determined to be in the range (0.18-0.29 eV). The photo-conducting properties and spectral response of the photodetector (made from the single crystal) were obtained and analyzed. The maximum spectral response of the detector was occurred at a wavelength of (720nm).

**$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$**

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(10<sup>-1</sup> torr)

Slow cooling  $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$

.

P	Hall measurements	Mobility
(0.18-0.29	Photo - conductivity	. eV)
	Single crystal	
	. (720 nm)	Spectral response

### **Introduction**

The multinary semiconductor compounds have attracted much attention due to their very great importance in different electronic applications, such that photodetectors, light emitting diodes (LED'S), laser diodes and solar cells. The study of the optoelectronic properties of such compounds will give a clear picture for their appropriate technological applications (Yaseen,2000).

Diaz *et al* (Diaz,1988) have studied the electrical and optical properties of the compound  $\text{CuInSe}_{2x}\text{Te}_{2(1-x)}$  which has been prepared as thin films using vacuum evaporation technique, on different types of substrates. They found that the optical gap is changed in the range (1.3-1.6 eV) with changing the deposition rate. They have been investigated that the electronic transitions occurred in these thin films is direct transitions. The study of their electrical properties have shown P-type conduction and it will be change into N-type by annealing processes at a temperature higher than 673K.

Diaz *et.al.*(Diaz,1992) have also shown that the thin films of the quaternary compound  $\text{CuInSe}_{2x}\text{Te}_{2(1-x)}$  have a characterized energy gaps which are 0.86, 0.95, 1.26, 1.51, and 1.77 eV. They found that the carrier's mobility is vary in the range of 0.2-28.6( $\text{cm}^2/\text{V.s}$ ) depending on the growth condition for these thin films.

Taha (Taha,1997) prepared a chalcopyrite multinary semiconductor compounds with general form  $\text{Ag In}_x \text{Al}_{1-x} \text{Se}_{2y} \text{Te}_{2(1-y)}$  from their high purity elements (99.999%) using melt growth technique. He was studied their structural and optoelectronic properties. The study shows that all prepared

compounds have N-type conduction. The researcher found that the samples doped with Cd, Sn, and Bi have acceptor surface impurities with activation energy ranged between (0.02-0.043 eV). The traps depth for the compounds have been calculated through the study of transient photo conductivity.

In this paper we study the optoelectronic properties of the quaternary semiconductor compound  $\text{Cu}_{0.5} \text{Ag}_{0.5} \text{GaSe}_2$  prepared by slow cooling method and as thin films by vacuum evaporation and D.C sputtering methods. The photoconducting properties and spectral response of a photodetector made from the single crystal of this compound were obtained and analyzed.

### *Experimentals*

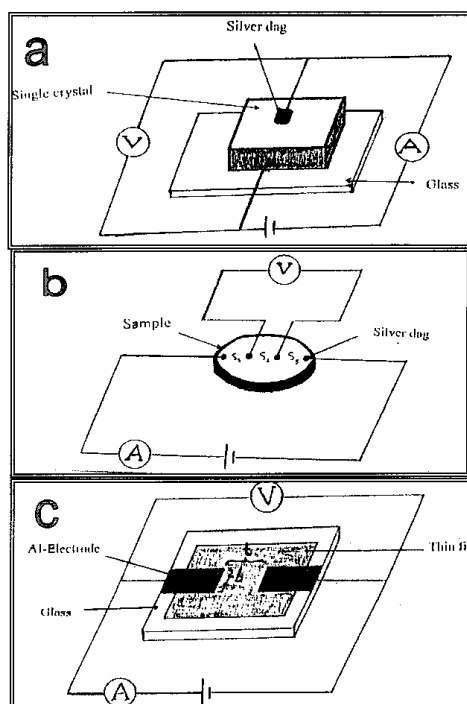
#### **Compound Preparation**

The quaternary compound  $\text{Cu}_{0.5} \text{Ag}_{0.5} \text{GaSe}_2$  was prepared by slow cooling method (2-3  $^{\circ}\text{C/hr}$ ) from their high purity elements(99.999%). A single crystal was obtained in the orientation (112) . The powder compound was used to prepare thin films by evaporation under vacuum and D.C sputtering methods. All samples were examined by X- ray diffraction and X- ray fluorescence, which showing that the compound powder is near stoichiometry with a chalcopyrite structure. The D.C sputtering method was applied in the potential differences 1.75, 2.0, 2.25 Kv under vacuume of  $10^{-5}$  torr and 6 mA anod current while passing of Ar gas(Taha,2003).

#### **Electrical conductivity Measurements**

The electrical measurements for all prepared samples (single crystal layer, bulk (as pressed disc) , and thin films) were carried out using the technologies (Rungon, 1975; Pouling, 1960; Abbas,1986) shown in Fig. (1)

The type of conductivity for thin films was obtained by Hall measurements and the mobility of charge carriers for these films was determined .



**Fig. (1)- The electrical technologies used for resistivity measurements .**

**a- a single crystal b-a pressed disc c- a thin film .**

**b-**

### **Optical Measurements**

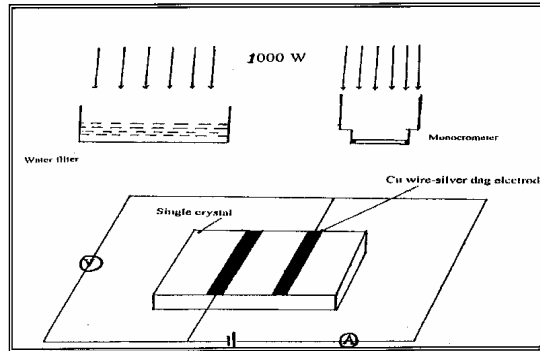
The optical absorption measurements for thin films were carried out using Pye Unicam Sp800 Spectrophotometer in the spectral range (400 - 900 nm) . The reflection measurements for thin films prepared by evaporation under vacuum were also obtained for different thickness samples ranged between (1.5-1.7  $\mu\text{m}$ ) . A solar spectrum reflectrometer (S.S.R) was used for this purpose .

### **Photoconductivity and Spectral Response Measurements**

The single crystal prepared by slow cooling of the compound was used as a photodetector after polishing. Ohmic contacts were done using two Cu wire fixed along the crystal by silver dag (Fig.2). The gap between the two wires was made as small as possible to reduce the path length of the charge carriers producing as a result of incident light. A tungsten source

(1000 watt) was used after calibration, and a water filter was placed in the path of the incident light to reduce the thermal effects (Taha,1983).

For measuring the spectral response of the detector a diffraction grating, type (Oriel – USA), was applied in the spectral range 300-900 nm.



**Fig. (2)- The electrical circuit diagram for measuring the photoconductivity and spectral response for the photodetector .**

**Results and Discussion.**

**Electrical Properties**

Figures (3) and (4) show the results of electrical conductivity ( $\ln\delta$ ) as a function of temperature in the range (298-498 K). These figures indicate a presence of two mechanisms of electronic transport in the temperature range used. The activation energies were determined using the relation (Nagat, 1990; Christman, 1988; Taha, 2002) :-

$$\sigma = \sigma_o \text{EXP}(-Ea / K_B T) \dots\dots\dots (1)$$

Where  $\sigma_o$ ,  $K_B$  are the pre exponential factor and Boltzman constants respectively,  $Ea$  is the activation energy, and  $T$  is the temperature .

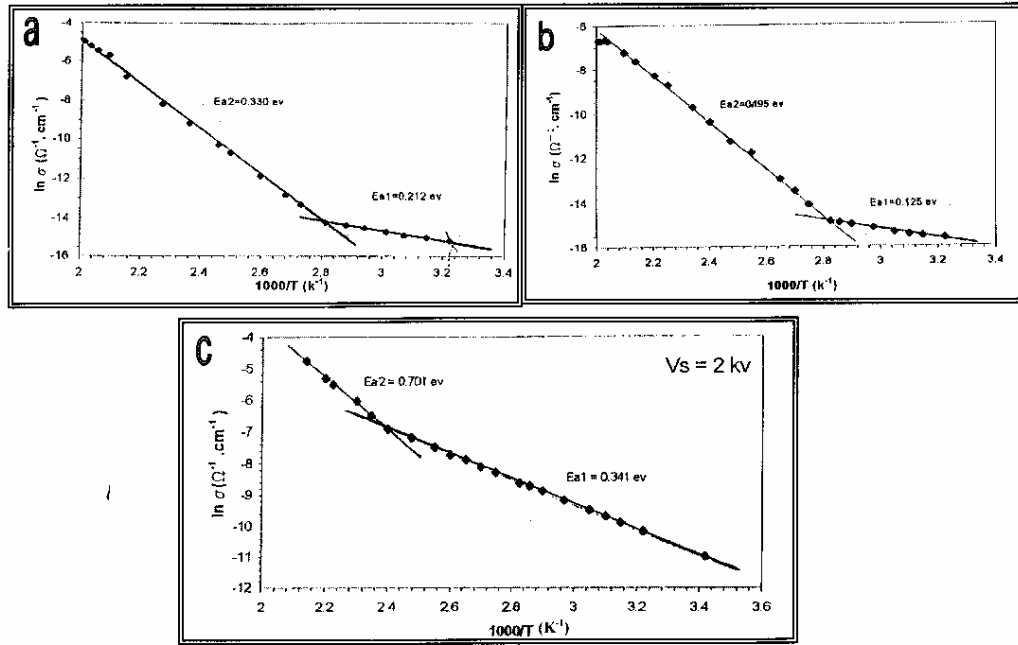


Fig. (3)- The electrical conductivity as a function of temperature .  
 a single crystal b- a pressed disc c- a thin film prepared  
 by D. C sputtering method .

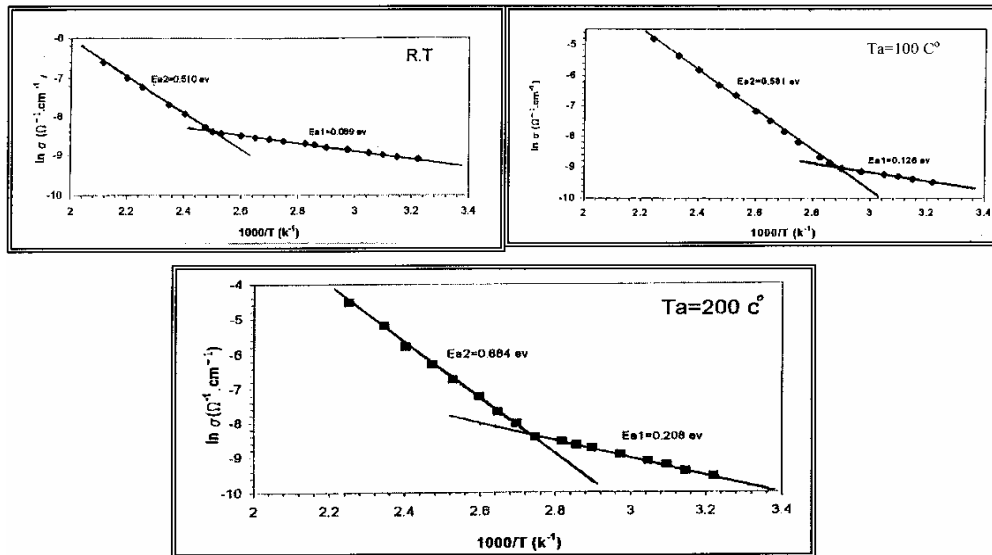


Fig. (4)- The electrical conductivity as a function of temperature for  
 a thin film prepared by vacuum evaporation method  
 annealed at different temperatures .

Table [1] indicates the results of electrical conductivity and activation energies for different samples of the compound  $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$ . The table shows clearly that the values of electrical conductivity for thin films (prepared by D.C sputtering and evaporation under vacuum) are greater than that of the single crystal or the pressed disc. This increasing in electrical conductivity can be explained due to the change in the stoichiometry of the prepared compound. This difference will lead to appearance of acceptor levels and then increasing in the charge carrier's concentration of P- type (Tuttle, 1989; Masse, 1986). Table [1] also shows the effect of annealing on the conductivity of the thin films prepared by evaporation under vacuum. The decreasing of electrical conductivity with increasing of annealing temperature may be explained due to the crystallinity increasing which leads to decrease in the localized states at the band edge (Lecomper, 1979; Mott, 1979; Al-Bachari, 1996).

**Table [1]- Results of electrical conductivity and activation energies for different samples of the compound  $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$ .**

$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$	$\sigma_{D.C} (\Omega.cm)^{-1} AT$	$E_{a1}(eV)$	$E_{a2}(eV)$
Single crystal	Chapter 2 $2.50 \times 10^{-7}$	0.212	0.330
Chapter 1 Pressed disk	Chapter 3 $1.60 \times 10^{-7}$	0.125	0.495
Thin film (R. T)	Chapter 4 $1.11 \times 10^{-4}$	0.089	0.510
Thin film( $T_a=100^\circ\text{C}$ )	Chapter 5 $7.40 \times 10^{-5}$	0.126	0.581
Thin film( $T_a=200^\circ\text{C}$ )	Chapter 6 $7.04 \times 10^{-5}$	0.209	0.684
Thin film( $V_s=2\text{Kv}$ )	Chapter 7 $1.67 \times 10^{-5}$	0.341	0.701

Hall measurements indicated that the prepared films are p-type. The annealing processes at the temperature range 298-498 K are not change the type of conductivity of thin films but lead to increase the carrier's mobility, as shown in table [2].

**Table [2]- Hall measurements for thin films of the compound Cu<sub>0.5</sub> Ag<sub>0.5</sub> GaSe<sub>2</sub> prepared by vacuum evaporation at different annealing temperature .**

<b>Cu<sub>0.5</sub>Ag<sub>0.5</sub>GaSe<sub>2</sub></b>	<b>R<sub>H</sub>cm<sup>3</sup>/c</b>	<b>P hole/cm<sup>3</sup></b>	<b>μ<sub>H</sub> cm<sup>2</sup>/v.s</b>
Thin film (R.T)	Chapter 8 <b>1.05×10<sup>4</sup></b>	Chapter 11 <b>5.90×1</b>	1.165
Thin film (Ta=100 <sup>0</sup> C)	<b>Chapter 9 1.35×10<sup>4</sup></b>	<b>0<sup>14</sup></b>	0.999
Thin film(Ta=200 <sup>0</sup> C)	<b>Chapter 10 1.61×1</b> <b>0<sup>4</sup></b>	<b>Chapter 12 4.6</b> <b>0×10<sup>14</sup></b> <b>Chapter 13 3.8</b> <b>8×10<sup>14</sup></b>	1.506

**Optical Properties**

The absorption coefficients (α) of the thin films have been estimated according to the relation : (Taha, 2001; Anwar, 1997; Hanna, 1992; Abass, 1987)

$$\alpha = \frac{2.303}{t} [A + \log(1 - R)^2] \dots\dots\dots (2)$$

Where *t* is the films thickness, A and R are the absorbance and reflectance respectively. After correction for the reflection losses, equation (2) can be reduced to :

$$\alpha = \frac{2.303}{t} (A - A') \dots\dots\dots (3)$$

Where *A* is the value of absorption corrections . The variation of the absorption coefficient with photon energy for a direct allowed band to- band transition is of the form (Anwar, 1997; Hanna, 1992 ; Abass, 1987)

$$\alpha_d h \nu = c (h \nu - E_{g_{opt}})^{1/2} \text{ for } h \nu \geq E_{g_{opt}} \dots\dots\dots (4)$$

$$= 0 \text{ for } h \nu < E_{g_{opt}}$$

Where α<sub>d</sub> is the absorption coefficient for a direct transition .

Fig. (5) shows the relationship of (hν<sup>2</sup>α)<sup>2</sup> vs. hν from which the optical energy gaps for direct allowed transitions for the thin films were calculated.



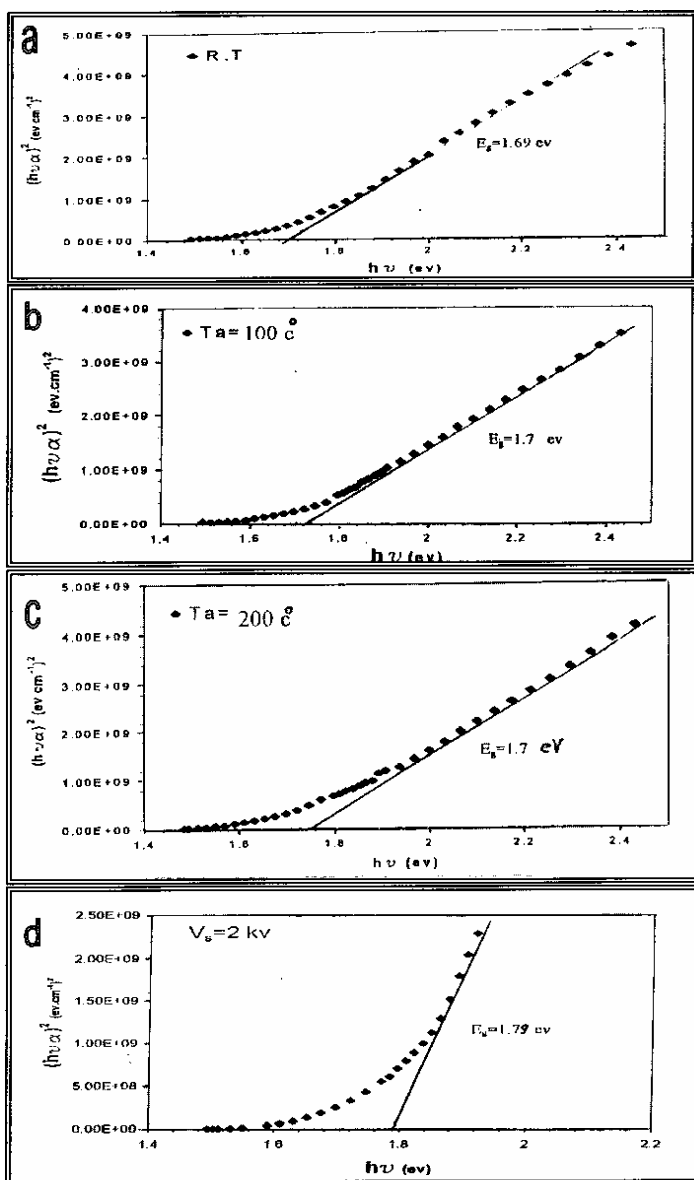


Fig. (5)- The optical energy gaps for direct allowed transitions for the thin films prepared at different conditions.

a, b, and c- are thin films prepared by vacuum evaporation annealed at different temperatures.

d- a thin film prepared by D. C sputtering at voltage source  $V_s = 2Kv$

Tails width of the localized states for this films were also calculated (Urbach tails) . The tail’s width values ( $E_t$ ) have been estimated according to the relation (Smith, 1978) :-

$$\alpha = \alpha_0 \text{EXP}(h\nu / E_t) \dots\dots\dots (5)$$

Table [3] lists the values of optical energy gap and the tail’s width for thin films. The table also shows that Urbach tails are occurred in the range of amorphous semiconductors (0.05-0.8 eV). It is also clear that these tails are decrease with increasing annealing temperature which is agree with absorption calculations .

**Table [3]- Energy gap values and tail’s width for thin films of the compound  $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$**

$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$	$E_{g_{opt}}$ (eV)	$E_t$ (eV)
Thin film (R.T)	<b>Chapter 14</b>	<b>Chapter 16</b>
Thin (Ta=100 <sup>0</sup> C)	<b>.69±0.02</b>	<b>.295</b>
Thin film(Ta=200 <sup>0</sup> C)	1.72±0.02	0.246
Thin film(Vs=2kv)	<b>Chapter 15</b>	<b>Chapter 17</b>
	<b>.79±0.02</b>	<b>.200</b>

In order to know the reflectance to the solar spectrum of the prepared thin films, reflection studies were carried out on thin films with thickness (1.50-1.70  $\mu\text{m}$ ). Table [4] lists reflection values in the solar spectrum regions. These results show that the reflection values are small specially in the maximum solar spectrum (0.4-0.6  $\mu\text{m}$ ), which make these films appropriate for solar cell applications .

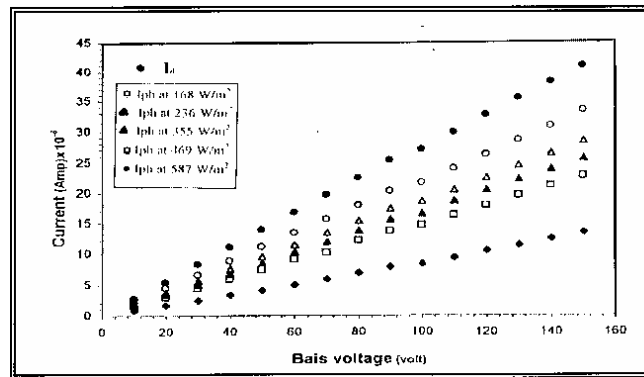
**Table [4]- Reflection values for thin films prepared by vacuum evaporation in the solar spectrum region.**

$t(\mu\text{m})$	<b>IR</b> 0.9 – 2.5 $\mu\text{m}$	<b>Red</b> 0.5 – 0.9 $\mu\text{m}$	<b>Blue</b> 0.4 – 0.6 $\mu\text{m}$	<b>Uv</b> 0.3 – 0.4 $\mu\text{m}$
1.70	0.120	0.071±0.004	0.027±0.004	0.001
1.60	0.088	0.075±0.004	0.031±0.004	0.001
1.50	0.075	0.075±0.004	0.036±0.004	0.001

### 3.3 Photoconductivity and Spectral Response of the photodetector

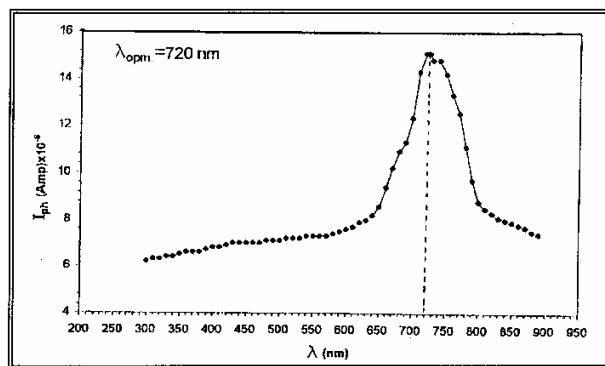
The photoconducting properties of the fabricated photodiode have been studied at room temperature. Fig. (6) shows the variation of a dark current ( $I_d$ ) and a photo current ( $I_{ph}$ ) versus different bias voltages at different illumination levels. The illumination levels have been calibrated according to a pyranometer (type CM 10) .

The gain has been calculated through intensities in the range (170-575  $w/m^2$ ) . Gain values were ranged between 1.68 to 3.04 This type of behavior is appear in the photo-sensitive materials in which the optical activation make to generate of excess electron – hole pairs (Neamen, 1992).



**Fig. (6)- Variations of a dark current ( $I_d$ ) and a photo current ( $I_{ph}$ ) versus different bias voltages at different illumination levels.**

Fig. (7) presents the spectral response of the photodetector. The maximum response is occurred at the wavelength 720 nm which is the optical energy gap of the compound (1.72 eV) .



**Fig. (7)- Spectral response of the photodetector.**

### *Conclusions*

From this study a general conclusions can be drawn :

- 1- Results of electrical conductivity measurements of the  $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{GaSe}_2$  compound indicated a presence of two mechanisms of electronic transport in the temperature range (298 – 498 K) .
- 2- Hall measurements show that all samples of the compound are P-type and the annealing treatment at the temperature range 298 to 498 K does not change the type of conductivity but lead to increase the carrier's mobility of the thin films .
- 3- Analysis of optical measurements indicated that electronic transitions occurred in the thin films of the compound is direct allowed transitions
- 4- Reflection measurements on to the thin films samples in the solar spectral region show small reflection values specially in the maximum solar spectrum region (0.4–0.6  $\mu\text{m}$ ) which make the compound to be convenience for solar energy applications .
- 5- The single crystal of the compound can be applied as a photo detector in the NIR region, specially at a wavelength 720 nm .

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