

***Study on The Effect of Annealing On The Optical Properties of The Pure Lead Sulfide (PbS) Films and Doping by Copper***

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### **Abstract**

Lead Sulfide (PbS) thin films were prepared by spraying pytolysis Method (SPM). Glass substrates with (1 x 2.6 x 7.6) cm were used at room temperature . Thin film of (PbS) was a doped by (Copper ,Cu) then the effect of annealing at different temperatures(100,200)C<sup>0</sup> on the optical properties of (pbS) and (PbS:Cu) are investigation.

The optical properties of the (pbs)and (pbs:cu) such as absorbance and transmittance have been analyzed by using (FTIR - 8400S) instrument. The optical band gab energy has been obtained from the plot between the ( $\alpha h\nu$ ) as a function of photon energy ( $h\nu$ ) was (0.43) eV for (pbs) and (0.41 ) eV for (pbs:cu) at the room temperature . The absorption spectra of the films showed that (pbs) and (pbs:cu) have a direct band gap increase slowly with temperature annealing

**Key Word : Optical Properties of Thin Films**

### **1 - Introduction**

Thin films are layers of material, It's have thickness about 1  $\mu\text{m}$  <sup>(1)</sup> .Because it is thin and fragile it deposited on a solid material such as glass, silicon or some salts or polymers<sup>(2)</sup>.

Thin films were raised the attention of scientists for more than a century, In 1857 Faraday could prepared metal films by evaporating metal wire in a vacuum by the passage of an electric current through it <sup>(3)</sup>, In 1876 he could prepare thin films adjacent to the layer of platinum and study the optical and electrical properties to this layer.

Intensive and expanded researches are continues to identify the properties of semiconducting materials , installation and construction ( crystalline ) . The possibility of making the most of them in practice , The results of this research were that manufacture of Rectifiers ,diodes , Photodiode and transistors <sup>(4)</sup>.

The lead sulfide (PbS) is a compound semiconductor with a dark color diagonal to the blackness <sup>(5)</sup> and has the properties of connectivity light which is very good at arange (800 - 3000 nm) at room temperature and has band gap energy directly up ( 0.40 eV) according to the World Tag (ASTM), making it suitable for the manufacture of photovoltaic cells connectivity which is used for military and civilian applications alike <sup>(6)</sup>

Copper is the metal with a red color reflects light red , orange and absorbs the rest of the wavelengths of visible electromagnetic waves and this is what gives red color

and distinctive features vulnerability on the roads and electrical and thermal conductivity is good <sup>(7)</sup>

## 2 - theoretical part

Lambert could describe the relationship between the intensity of the incident light ( $I_0$ ) and the intensity of light transmission ( $I_t$ ) as the following

$$I_t = I_0 e^{-\alpha x} \dots\dots\dots (1)$$

where

(t) is a thickness , ( $\alpha$ ) absorption coefficient <sup>(8)</sup> which can be defined as the percentage decrease in radiation energy per unit distance towards the wave propagation inside the medium , The absorption coefficient depending on the photon energy of the incident wavelength , the nature of the thin film surface of the semiconductor , the properties of the semiconductor (band gap energy ) and the type of electronic transitions within the energy band <sup>(9), (10)</sup>

The value of the absorption coefficient is determine the type of transitions where the ( $\alpha > 10^3 \text{cm}^{-1}$ ) means direct transitions, while ( $\alpha < 10^3 \text{cm}^{-1}$ ) means indirect transitions <sup>(11)</sup> .

The ratio ( $I_t/I_0$  ) is called transmittance and represents the intensity of light transmission through thickness ( t ) . The relationship between transmittance and absorbance can be shown as the following <sup>(12)</sup>

$$A = \text{Log } (I_0/I_t) = \text{Log } 1 / T \dots\dots\dots (2)$$

$$\text{Ln } (I_0 / I_t) = \alpha t \dots\dots\dots (3)$$

$$\alpha t = 2.303 \text{ Log } (I_0/I_t) \dots\dots\dots (4)$$

$$\alpha = 2.303 A / t. \dots\dots\dots (5)$$

Equation (5) shown that a primary factor in the conclusion band gap is the absorption coefficient where by using the following equation

$$E = h\nu \dots\dots\dots (6)$$

And in terms of the wavelength take equation (1) as follows:

$$E \text{ (eV)} = (hc / \lambda) = (1240 / \lambda) \dots\dots\dots (7)$$

where h : Planck's constant , C the velocity of light in a vacuum <sup>(9)</sup>, and sketch the plot of  $(ah\nu)^2$  versus  $(h\nu)$  was analyzed by using the following equation

$$\alpha = k (h\nu - E_g)^{n/2} / h\nu \dots\dots(8)$$

where k is a constant, and n is a constant which depends on the type of transition (n =1/2,2,3/2 and 3) corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively.. Extrapolation of the linear portion of the plot to the energy axis yielded the direct band gap value for thin film<sup>(8)</sup>

## 3 – Experimental Details

Pure (pbs) thin film and doped by (.30cu) were prepared by spraying pytolysis Method (SPM), Its efficiency and low cost, addition to this method have been used extensively to study the physical properties of many materials in the form of thin films .

This method can be explained in the following steps before the deposition process thin films on the glass substrates with (1 \* 2.6 \* 7.6) cm.

First: The contents of the unit coverage are clean to get rid of the sediment material by using special paper with high-purity alcohol before the closure of the unit coverage and make the process of unloading until we are getting on the desired pressure .

Second: cleaning the glass substrates by a solution (10% oily substance type (RBS50) with (90%) of distilled water and then placed in the ultrasonic device for a period of 15 minutes.

Third, the glass substrates are drying by using oven for a period of (10 min) at temperature (30C °).

Fourth, keep the glass substrates in a plastic containers.

Fifth, make sure that the system is empty from the air by using a pump (rotary pump  $10^{-2}$  mbar).

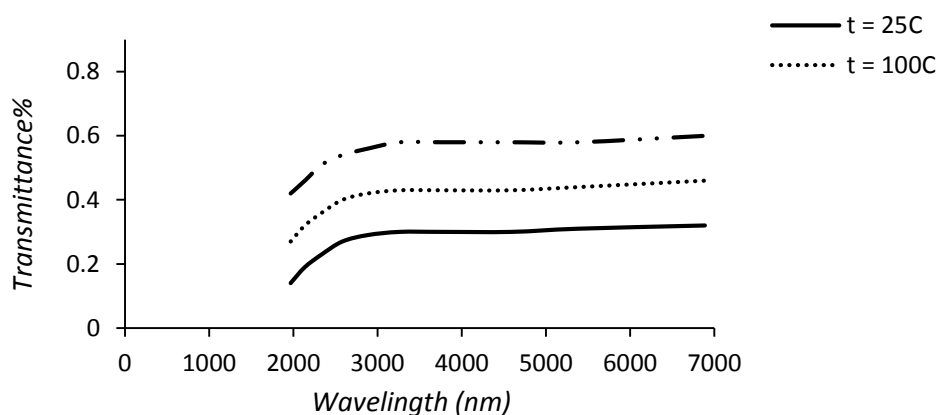
Sixth: put the material inside the Boat, while the glass substrates are placed in the other hand of the system

Seventh: The material is smelted by using electric current pass through the Boat, on distance  $R = (17 \pm 1)$  cm of the glass substrates ,the spray rate was about  $15\text{cm}^3/\text{min}$ .

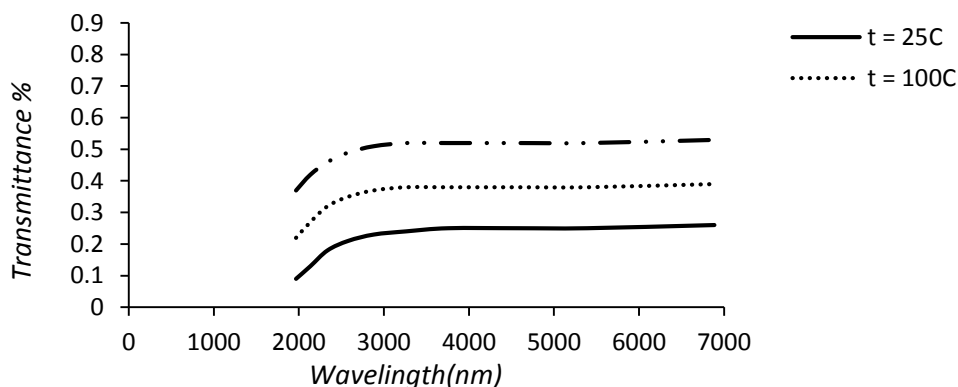
## 4 - Results and Discussion

### 4 - 1 measurements of transmittance

The variation of transmittance as a function of wavelength for the (pbs) and (pbs:cu) thin films at a different temperature annealing (25, 100, 200) C<sup>0</sup> is show in Figures (1a) and (1b) respectively



**Figur (1a): Transmittance Spectra at a Various Temperatures for (PbS) Thin Film**

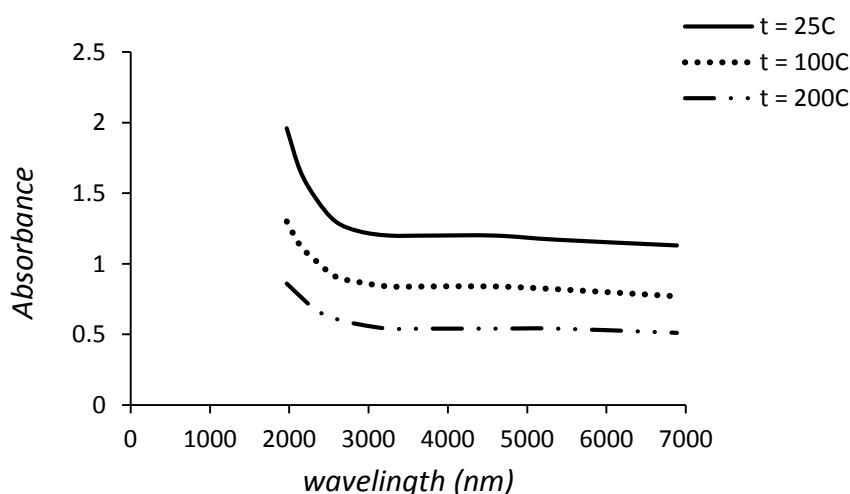


**Fig. (1b) Transmittance Spectra at a Various Temperatures for (PbS:Cu) Thin Film**

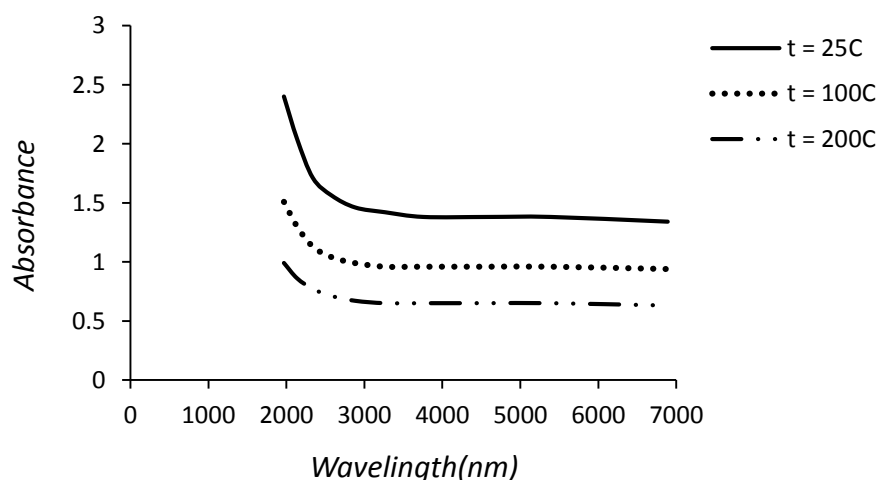
Figures in above shown that the films have transmittance less than (20%) of the ( $\lambda > 2000$  nm) at room temperature ,but its increase to reached to more than (40% ) in the range ( $\lambda < 2000$  nm) for all temperatures of the annealing . Also it can be observed from Figure (1b) that the transmittance will decrease at doped pure (pbs) films by copper, where The transmittance is ( 60% ) at (200C) for the pure thin film while its ( 53% ) for the film doped by copper, This improvement can be attributed to the fact that annealing lead to increase the energy gap as a result to the disposal of some crystal defects or increase the growth of grain size .

**4- 2 absorbance measurements**

Optical absorption studies of the (pbs) and (pbs:cu)films have been carried out in the wavelengths range between (1500 -7000)nm and are shown in Figures (2a) and (2b)



**Fig.(2a) Absorbance Spectra at a Various Temperatures for (PbS) Thin Film**



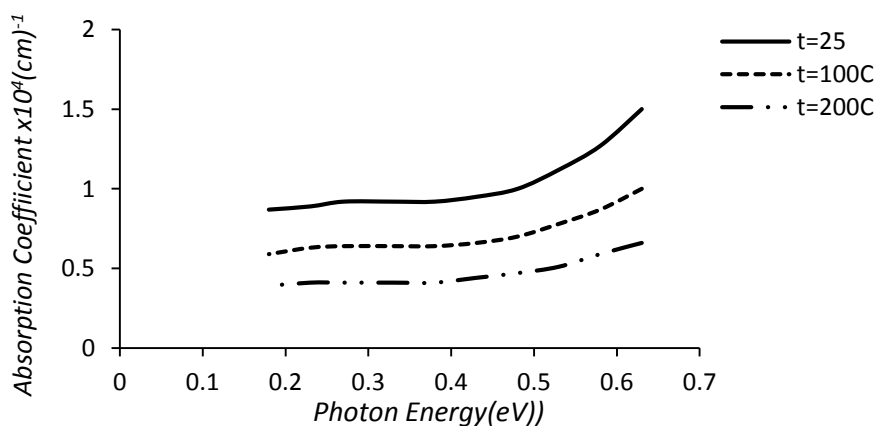
**Fig. (2b) Absorbance at a Various Temperature for (PbS:Cu) Thin Film**

Figure (2a) shown that the behavior of the absorbance curve as a function of wavelength is inversed to the behavior of the transmittance

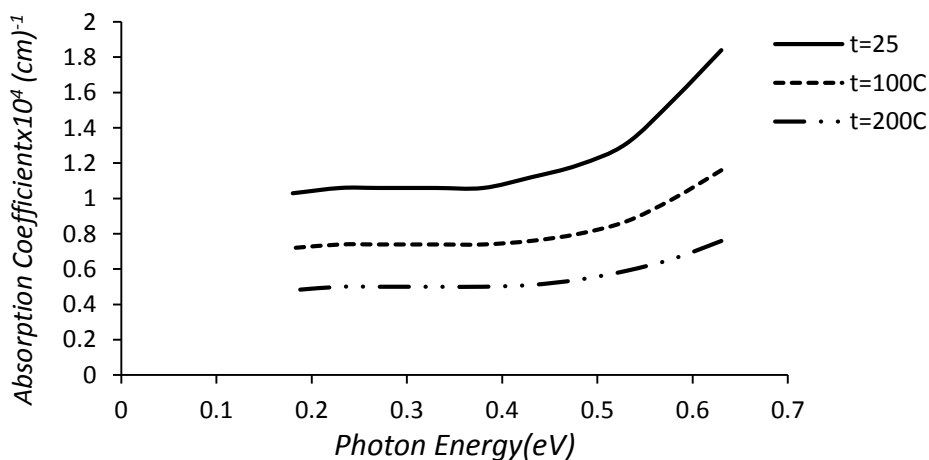
It can be observed that in general, there is a decrease in absorbance up less than (5%) in the range ( $\lambda > 2000$ ) for pure (pbs) thin films and (pbs:cu). That it means that annealing of the thin films lead to decrease absorption coefficient , as shown in Figures (3a, 3b). Also it can be observed from Figure (2b) increased absorbance for (pbs:cu) thin film reached to ( 2.4 ) in the range ( $\lambda < 2000$ ) while absorbance for the pure (pbs) thin film was (1.96) at the same range of wavelength ,but this increase will be low at increase of annealing , which means that the transmittance a decrease as shown that Figures (1a) and (1b)

### 4 - 3 absorption coefficient measurements

The absorption coefficient of the films have been calculated from the experimentally measured values of absorbance and transmittance according to the equation (1) where ( $t = 300\text{nm}$ ). Absorption coefficient spectra versus the incident photon energy for pure (pbs) and (pbs:cu) are presented in Figures(3a) and (3b)



**Fig.(3a): Absorption Coefficient As a Function of The photon Energy for (PbS) Thin Film**



**Fig. (3b): Absorption Coefficient As a Function of The Photon Energy for (PbS:Cu) Thin Film**

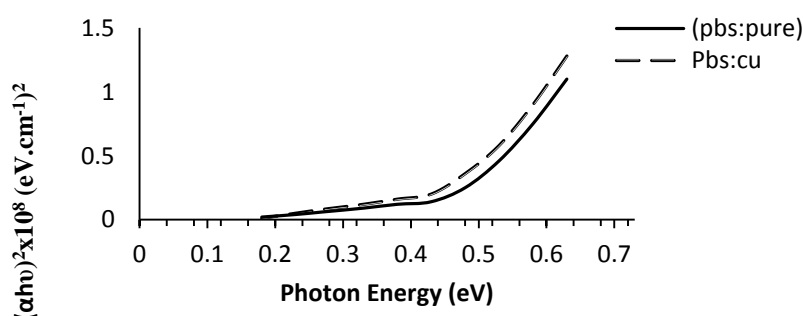
Figures(3a) shown that the (pbs) films have a low absorption coefficient at annealing, But at band gap(0.43eV) absorbance coefficient is increasing rapidly, This behavior of the absorption coefficient curve may be due to increase crystallized material , which in turn reduces crystal defects , as well as its leading to reduced levels of topical within the forbidden band gap energy caused by a defect in the crystal structure .

Figure (3b) shown that absorption coefficient is increased at doped pure (pbs) films by copper, Also it can be observed from Figures (3a,3b) that all the transfer of the (PbS) thin films and doped with copper are the direct electronic transitions where values of the absorption coefficient ( $\alpha > 10^3 \text{ cm}^{-1}$ ).

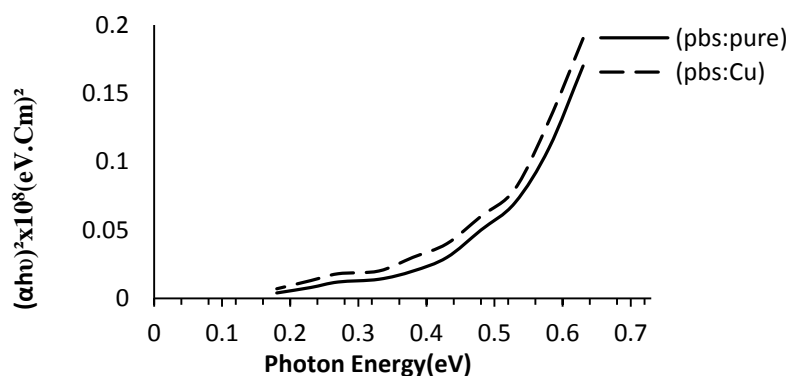
#### **4 – 4 Determination of the gab energy**

The optical band gap for the films was determined by analyzing the optical data with the expression for the optical absorbance ( $\alpha$ ) and the photon energy ( $h\nu$ ) using the equation (8)

Figures (4a) and (4b ) shown that the plot of  $(\alpha h\nu)^2$  versus  $(h\nu)$  was analyzed by using the equation (8). Extrapolation of the linear portion of the plot to the energy axis yielded the direct band gap value, Its equal to (0.43, 0.41) ev for (pbs) and (PbS:Cu) thin films at room temperature respectively and varies from (0.43 - 0.45) eV at annealing (100) C for (PbS) thin film . It has attributed the reason for this to get rid of blemishes or growth of crystalline grain size



**fig.(4a): Relationship Between  $(\alpha h\nu)$  and Photon Energy at Room Temperature**



**Fig(4b): Relationship Between  $(\alpha h\nu)$  and Photon Energy at (100)c**

Figure (4a) shown that when (pbs) thin films were doped by copper at room temperature then value of band gab will be reduced slightly, but its increase a slight at annealing of the films to reached to (.41 -.43) eV at a temperature annealing (100) C Fig.(4b) shown that .

### **5- Conclusions**

Films of (pbs) and (pbs:cu) on to glass substrate have been prepared by using aspray pyrolysis method. The optical studies reveal that

- 1 . We get that increasing at all the optical properties after doped by copper but decreasing in transmittance. Which means that the effect doping on (PbS) thin film is positive .
- 2 . The pure (PbS) thin film and doped with (cu) have low transmittance in the (IR) region but its increasing at annealing
- 3 - The pure (pbs) thin films has a direct narrow band gab (0.43)eV and (.41 )eV with doping by copper, It is observed that the band gab increasing at annealed, But its decreases by doping
- 4 . Through the calculated values of the absorption coefficient we found that all the transfer of the (PbS) thin films and doped with (cu) are the direct electronic transitions .

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## دراسة حول اثر التلدين على الخواص

### البصرية لغشاء كبريتيد الرصاص (PbS) النقي والمشوب بالنحاس

تاريخ الاستلام :

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### الخلاصة

تم في هذا البحث قياس بعض الخواص البصرية لغشاء (PbS) النقي و المحضرة بطريقة الرش الكيميائي الحراري وذلك بترسيب الغشاء على قواعد زجاجية وبأبعاد  $7.6 \times 2.6 \times 1$  cm وبدرجة حرارة الغرفة وتشويب الغشاء بالنحاس ودراسة أثر التلدين عند الدرجات الحرارية ( $100^{\circ}\text{C}$  ،  $200^{\circ}\text{C}$ ) على تلك الخواص للغشاء النقي والمشوب تم قياس خواص الامتصاصية والنفذية للأغشية بواسطة جهاز (F.T.I.R - 8400S) وتحليل البيانات البصرية الخاصة بمعامل الامتصاص وطاقة الفوتون الساقط أمكن رسم العلاقة بين ( $\alpha h\nu$ ) كدالة لطاقة الفوتون ( $h\nu$ ) تم حساب فجوة الطاقة البصرية للغشاء النقي والمشوب وقد تبين إن هذه الفجوة هي فجوة طاقة مباشرة تبلغ قيمتها ( $0.43$  eV) بالنسبة للغشاء النقي و ( $0.41$  eV) للغشاء المشوب بالنحاس وتزداد هذه القيمة بشكل بطيء مع درجة حرارة التلدين .

**الكلمات المفتاحية: الخواص البصرية للأغشية الرقيقة**