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Preparation of lead sulfide films doped with different ratios of copper and their characterization

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Abstract:

Lead sulfide (PbS) films were prepared with different copper doping ratios (0%, 2%,4%,6%) under (55) C° using the chemical bath deposition method (CBD). The results of X-ray showed that all the doping films are polycrystalline and have a cubic structure, where the crystallization process is good at plane (200) for the doped film at a ratio of 2%. The greatest value of the grain size is at the doping ratio of 2% and its values decrease with the increase in the doping ratios, just as the density of dislocations decreases at the percentage of 2% and its values increase with the increase in the doping ratios. The results of UV-Vis proved that transmittance increases with increasing the doping ratios and with decreasing the thickness of the doped film. From calculating the values of the energy gap for the prepared films, It was found that their values increase with increasing doping ratios resulting from a decrease in crystalline defects.

Key word: PbS films, copper doping, chemical bath deposition method.

تحضير اغشية كبريتيد الرصاص المطعمة بنسب مختلفة من النحاس وتوصيفها

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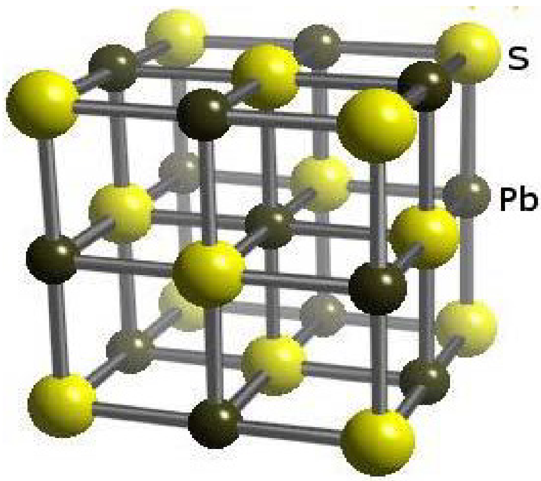
مستخلص:

تم تحضير أغشية كبريتيد الرصاص (PbS) بنسب تطعيم مختلفة من النحاس (0٪ ، 2٪ ، 4٪ ، 6٪) تحت درجة حرارة (55 C°) باستخدام طريقة الترسيب بالحمام الكيميائي (CBD) ، أظهرت نتائج حيود الأشعة السينية أن جميع الاغشية المطعمة متعددة التبلور وذات بنية مكعبة ، حيث كانت عملية التبلور جيدة عند المستوى (200) للغشاء المطعم بنسبة 2٪. وتكون اعلى قيمة للحجم الحبيبي عند نسبة تطعيم 2٪ وتتناقص قيمها بزيادة نسب التطعيم، كما ان كثافة الانخلاعات تتناقص ايضا عند نسبة 2٪ وتزداد قيمها مع زيادة نسب التطعيم. أثبتت نتائج UV-Vis أن النفاذية تزداد بزيادة نسب التطعيم مع تناقص سماكة الغشاء المطعم. ومن حساب قيم فجوة الطاقة للأغشية المحضرة تبين أن قيمها تزداد بزيادة نسب التطعيم الناتجة عن نقصان العيوب البلورية .

الكلمات المفتاحية : اغشية PbS ، التطعيم بالنحاس ، طريقة الحمام الكيميائي .

1- Introduction:

Lead sulfide (PbS) is a black inorganic chemical compound. It is a toxic compound when heated to the point of disintegration due to the formation of lead oxides and sulfur oxides. PbS tends to crystallize as sodium chloride (NaCl) with a concentric cubic structure. The faces are FCC, with a lattice constant of about (5.936) Å [1].as shown fig (1).



Fig(1) Primary cell of a lead sulfide crystal [2]

PbS is one of the promising compounds due to its optical and distinctive electrical and structural properties and its many and varied applications. It has high quantum efficiency, and a fast response time [3.4]. PbS is a semiconductor and belongs to group (VI-IV), as it has photoconductive properties. [5]. PbS has a narrow, direct energy gap (0.4 eV) at 300 k^{o}, and Bohr radius18 nm exciton [6] which makes it very suitable for infrared detection applications [7]. It also has an absorption coefficient that increases continuously from the infrared to the visible range. [6], PbS is used in photography, a transition sensor for Pb^{+2} lead ions in solar cells, a photoresist, a humidity sensor, a temperature sensor , and a radio wave detector [7]. Thin film technology is considered one of the most important techniques used in the development of the study of semiconductors and their properties because the thin film layer is deposited on different materials such as glass, silicon and metals.[8] Thin films are also used in the manufacture of components for thin electrical appliances, reagents, and the manufacture of mirrors and panels sensitive to electromagnetic waves. Because of their small size and light weight, they have entered the field of building digital electronic computers and in the development of space research equipment [9]. There have been many methods for preparing thin films, and each method has its advantages and characteristics in order to obtain films of purity, accuracy and control over the thickness and homogeneity of the films. Such as the pulsed laser ablation deposition method (PLAD) [10,11] In this research, the chemical bath deposition method was used to prepare PbS films, as it is a simple method that does not require high temperatures or high pressure, and is also used with different characteristics such as changing the sedimentation time, temperature, raw material concentrations, and complexing agent concentration.[12]

2- Experimental part:

The chemical bath precipitation method was used by dissolving (1.416) g of lead acetate $Pb(CH_3CooH)_2$ as a source of lead ions (Pb^{+2}) at a concentration of (0.05)M at room temperature in (22.5) mL of distilled water and placed with a magnetic mixer for (10) min. Then, (2.5) mL of a complex triethanol-amine solution (C_2H_7NO) is placed on it, while continuing to mix. A thiourea solution, $Cs(NH_2)_2$, was prepared as a source of sulfide ions (S^{-2}) by dissolving (0.38)g in (25) mL of distilled water with a concentration of (0.1)M at room temperature using magnetic mixing for a period of (10) min. $Cs(NH_2)_2$ solution is added to C_2H_7NO + $Pb(CH_3CooH)_2$ solution with continuous mixing. After that, a copper acetate solution is prepared as a source of Cu by dissolving (0.25) g of the solution with a concentration of (0.05) M in (25) mL of distilled water and placing it in the magnetic mixer, where the solution turns blue. The prepared lead acetate solution is withdrawn and replaced by copper acetate with doping rates of (0%, 2%, 4%, 6%). After that, the first glass substrate is placed after being thoroughly cleaned and dried vertically in the prepared sedimentation solution at the percentage (0%) at a temperature (55) C^o and with a sedimentation time of (60) min. The color of the sedimentation solution changes from brown to black [13] and when the sedimentation is complete, we take out the substrate, wash it, and then dry it with the same work for the second substrate at (2%), the third at (4%), and the fourth at (6%).

3. Results and discussion:

3.1 Structural properties:

X-ray diffraction of the prepared PbS shows that the material has a polycrystalline structure and have a cubic structure as in figure (2) and there are no impurity peaks. This confirms the purity of the doping material [14,15]. The peak (200) appears at (2Θ = 30.05°) in the film with the doping ratio of 2% was the highest and its intensity decreased in the other films with increasing doping ratio. The peak (200) represents the preferred direction of film growth, as copper ions preferentially enter the plane (200) to change the relative growth rate of the crystal plane, as these ions enter the defect sites in the crystal, which enhances the crystallization process of the material [17]. This is consistent with the results published by researchers in previous studies [15]. The peak (111) appears in all films and decreases with increasing doping ratios in the other films. As doping ratio increase, the intensity of the main peaks decreases, and the crystal begins to deteriorate at an 8% doping ratio. This is because copper ions have a smaller ionic radius [16], because the copper ions have a small ionic radius, as they enter the defect sites in the crystal and work to enhance the crystallization process of the material [17].

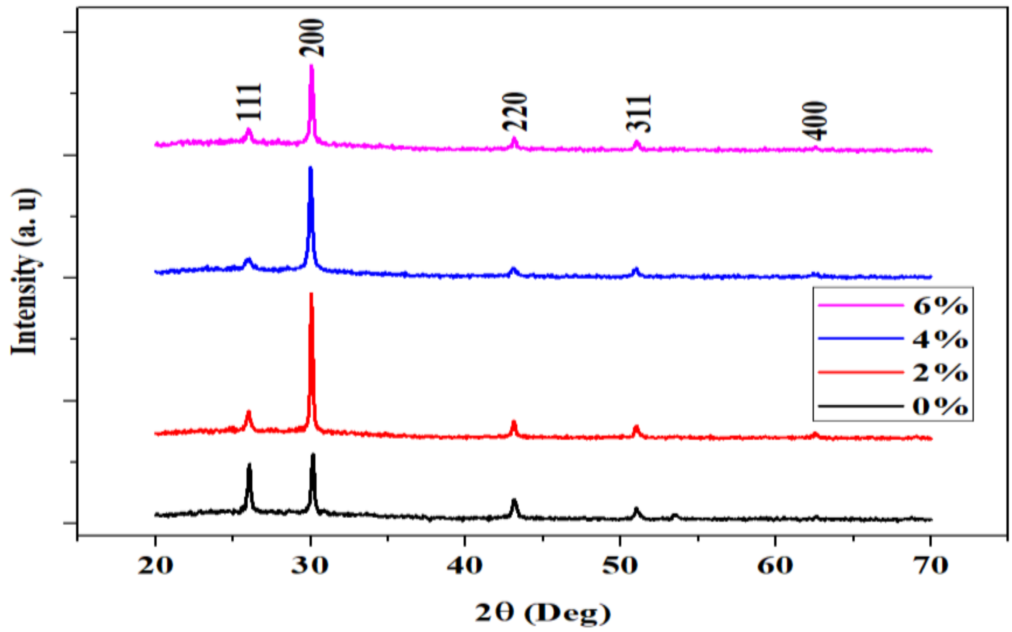


Fig.(2) X-ray diffraction of PbS films prepared with different copper doping ratios.

We find the average crystallite size (D_{av}) From the scherrer formula [18] for all films prepared in planes (111), (200), (220), (311).

$$D_{av} = \frac{0.9\,\lambda}{\beta\cos\Theta} \quad \text{............(1),}$$

where β= Full Width at Half Maximum (FWHM) of the diffraction peak, λ= wavelength of the X-ray and Θ= diffraction angle. Can be observed that the grain size. Table (1) shows that the grain size increases first to reach a maximum value at a doping ratio of 2%, this increase reduces the grain boundaries and thus reduces crystalline defects. Then the grain size decreases with an increase in the doping ratio with copper, as shown in figure (3), many believe that the introduction of copper restricts crystal growth [17].

Table (1) Shows the values of β, D_{av} in the planes (200),(111),(220),(311) of PbS films with different copper doping ratios.

Films (PbS)	hkl	FWHM $\beta.10^{-3}$	D (A^o)	D_{av} (A^o)
0%	(200)	5.1496	493.7	486.5
	(111)	3.43306	497.9	
	(220)	6.8661	516.9	
	(311)	5.1496	437.7	
2%	(200)	3.433	386.9	555.9
	(111)	3.433	696.4	
	(220)	3.433	722.8	
	(311)	4.291	417.7	
4%	(200)	4.291	318.8	352.1
	(111)	2.574	497.8	
	(220)	2.574	247.7	
	(311)	4.291	344.1	
6%	(200)	6.866	236.6	331.6
	(111)	3.433	497.8	
	(220)	6.866	247.8	
	(311)	5.149	344.3	

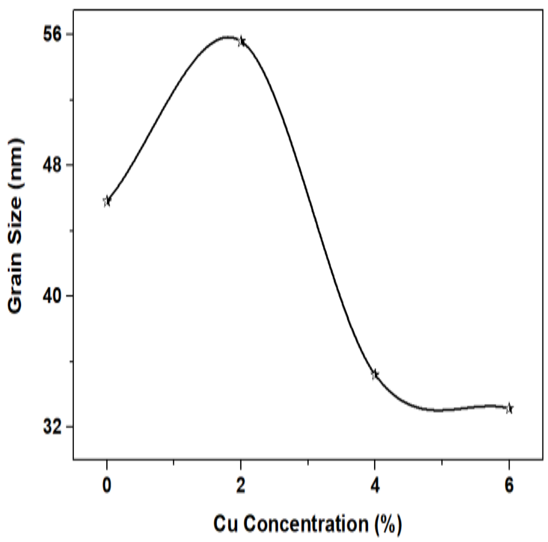


Fig. (3) Grain size of PbS films with different copper doping ratio.

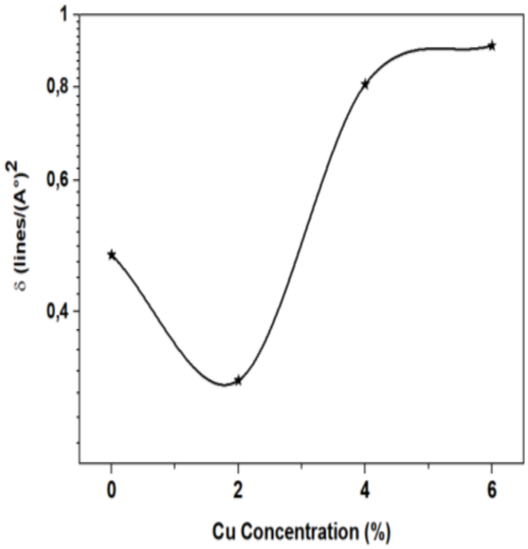


Fig.(4) Density of dislocations of PbS films with different copper doping ratio.

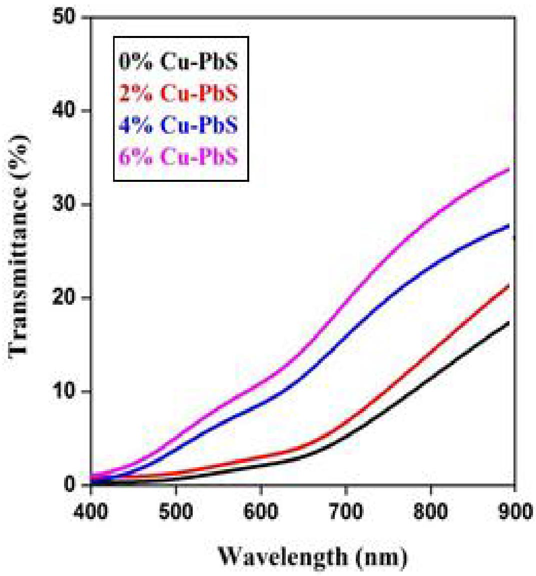
We also notice that the density of dislocations (δ) is represented by the following relationship [19],

$$\delta = \frac{1}{D_{av}^{2}} \quad \text{..........(2),}$$

The value (δ) of deceases at a dops ing rate of 2%. So, crystal defects decrease, and δ increases with increasing ratio of doping with copper, as in the figure (4).

3.2 Optical properties:

From the examination of UV-Vis, it was found that the values of transmittance of the prepared PbS films increase with the increase of the wavelength of all the films. the transmittance values are as low as possible within the ultraviolet radiation region within the range (300-400) nm and the transmittance values increase in the visible region within the range (400-700) nm to reach the highest peak within the range (700-900) nm. Therefore, the transmittance increases with the increase of the doping ratio [17,20] as shown in figure (5). Figure (6) shows the decrease in the thickness of the prepared PbS films by increasing the doping ratios. As the amount of copper increases, the reaction speed decreases and the thickness of the films decrease. Decreasing the thickness of the film increases its transmittance and reduces its absorption because the thin films contain fewer atoms to absorb photon energy [14, 20].



Fig(5) Transmittance spectrum of PbS films with different copper doping ratio.

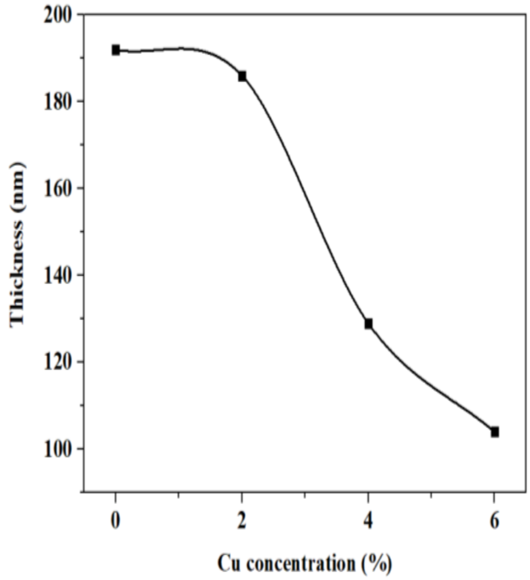


Fig.(6) Thickness changes of PbS films with different copper doping ratio.

The energy gap for the films prepared with different doping ratios found through the relationship between $(\alpha h\nu)^2$, $(h\nu)$,) appears in the figures (7 ,a,b,c,d) which show that the energy gap increases from (1.16) eV to (2.03) eV due to the doping from (0%) to (6%) [17]. This increase is due to the decrease in the thickness of the films which result from the decrease in the width of the local planes within the energy gap. Accordingly, the crystalline defects are reduced by increasing the doping ratios. [21].

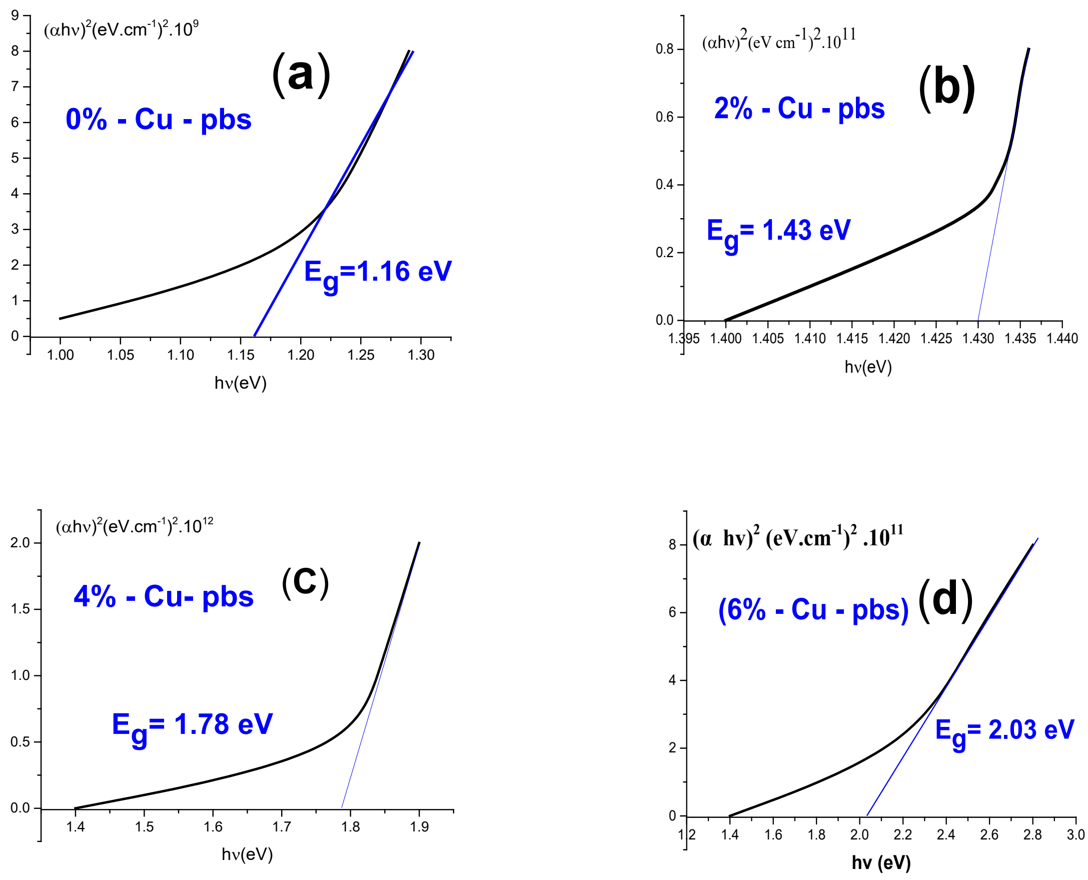


Fig. (7, a,b,c,d) Curves $(\alpha h\nu)^2$ in terms of hν for PbS films prepared with different copper doping ratios.

Table (2) Shows the values (E_g) for PbS films prepared with different copper doping ratios

Doping ratio %	0	2	4	6
E_g (eV)	1.16	1.43	1.78	2.03

Conclusion:

The results of X-ray diffraction showed that the films prepared for PbS are polycrystalline and have a cubic structure. The grain size of the prepared films increases to reach a maximum value and then decreases with the increase of the different copper doping ratios for the films. By examining UV-Vis it was found that the transmittance of the prepared films increases by increasing the different doping ratios, and the thickness of the films decreases with the increase in the doping ratio of the prepared films. Therefore, the decrease in the thickness of the film increases its transmittance and reduces its absorption. It was also shown that the energy gap of the prepared PbS films increases with the increase in different doping ratios of the films. The prepared PbS films have many properties and applications as in photovoltaic applications such as solar cells and photodetectors.

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