

Electrical and Structural Characterization of Thin Pb_{0.5}S_{0.5} Films Deposited with Different Thicknesses

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Abstract

Pb_{0.5}S_{0.5} alloy has been prepared successfully by the method of quenching for elements melt. The Pb_{0.5}S_{0.5} thin films of 200, 400, 600, 800 and 1000 nm thickness have been prepared from the prepared alloys by thermal evaporation technique onto glass substrate at room temperatures. The X-ray diffraction study shows that the prepared films are cubic polycrystalline structure with strong peaks at (200) and (111) planes, the intensity of the peaks increases with increasing film thickness. The grain size increases with increasing film thickness and their values varied between 35 and 59 nm. The D.C conductivity has been displayed two stages of conductivity through the whole temperature range. D.C conductivity have increased from 0.50×10^{-2} to 1.86×10^{-2} ($\Omega \cdot \text{cm}$)⁻¹ as film thickness increased. All prepared films have two activation energies, where these values decrease with increasing thickness. The maximum value of activation energy was 0.177 eV at 200nm thickness, and then decreased to 0.067 eV in thermal range 413-493K. Hall Effect results have been shown that all prepared thin Pb_{0.5}S_{0.5} films were p-type material. The carrier concentration increases with increasing thickness, and it varies from $0.079 \times 10^{19} \text{ cm}^{-3}$ to $9.55 \times 10^{19} \text{ cm}^{-3}$ for thickness from 200 to 1000nm. The Hall mobility has been decreased from 3.99 to 0.098 ($\text{cm}^2/\text{V} \cdot \text{sec}$) as thickness increased from 200 to 1000nm. The drift velocity of these films decreases with increasing this films thickness.

Introduction

Semiconductor materials are always in focus due to their outstanding electronic and optical properties [1]. Lead salts and their alloys have a number of interesting physical properties as well as numerous potential applications. Lead chalcogenides (PbS, PbSe and PbTe) exhibit some unusual and unique properties such as high dielectric constant, narrow energy gap and high mobility [2]. The most remarkable feature of this group of compound semiconductors is the relative stability of the lattice over a wide range of stoichiometry [2]. As an important IV-VI group semiconductor, lead sulphide (PbS) is an important direct narrow band gap semiconductor material ($\approx 0.41 \text{ eV}$ at room temperature) [1], a relative cut-off wavelength of $3 \mu\text{m}$ [2] and high absorption coefficient continuously increasing the infrared through the visible region [3]. PbS thin films have been used as ideal selective surfaces for photo thermal conversion application. It is important as electronic and optoelectronic devices, in infrared photography, photoconductive cells, photovoltaic cells, contact less thermometers [3], including light-emitting diodes, single

electron transistors, field effect transistors, Pb²⁺-ion-selective sensors, IR detector, photography and solar absorption [1, 3]. In addition PbS has been utilized as photo resistance, diode single electron transistors, field effect transistors, Pb²⁺-ion-selective sensors, IR detector, photography and solar absorption [1,3]. In addition PbS has been utilized as photo resistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings [1]. Laser diodes based on lead chalcogenides and their alloys act as an important source of tunable radiations in mid infrared wavelength region. They are widely utilized in advance measuring systems to detect hydrocarbon pollutants in atmosphere, high resolution spectroscopy, trace gas analysis and optical fiber communication analysis and optical fiber communication systems over long distances [4,5]. This material has been studied by various deposition techniques such as electro-deposition, spray pyrolysis, photo accelerated, chemical deposition, microwave heating, chemical bath deposition (CBD), and vacuum evaporation [6-9].

The aim of this work is to investigate the effect of variation of thickness on the structure and electrical properties of $Pb_{0.5}S_{0.5}$.

Experimental Work

High purity Pb and S element of 99.999% have been used to prepare $Pb_{0.5}S_{0.5}$ alloy according to the relative atomic weight of the elements, the component of the alloy have placed in quartz tube, which attached to evacuated system, the tube has been sealed at pressure 10-3 mbar and placed in electrical furnace which maintained at 1387K for several hours, after that the tub has been quenched rapidly in cold water. Thin films of 200, 400, 600, 800 and 1000 nm thickness have been prepared from this alloy on ultrasonically cleaned 7059 corning glass slides (of 1mm thickness) using deionized water and pure alcohol for 15 minutes [10]. The evaporation process has done under vacuum of 5×10^{-6} mbar at room temperature using Edward 306A vacuum coating system. The deposition rate was 0.8 nm/sec. The structure of the $Pb_{0.5}S_{0.5}$ films have been examined by Phillips X-Ray diffractometer, with source CuK_{α} radiation of the wavelength is 1.5405 Å, current 20 mA and Voltage 40KV. The electrical resistance has been measured by Keithley 616 digital electrometer as a function of the heating temperature (T) produced by Memert electrical oven for studying D.C conductivity. Hall effect has been measured by carrying a current expose a constant magnetic field ($B=0.254$) Tesla perpendicular to the electric field applied from D.C power supply (0-40)V, then the current (I) and Hall voltage (V_H) were recording by using Keithly Digital Electrometer 616.

Results and Desiccation

X-ray diffraction studies

The structure of thin $Pb_{0.5}S_{0.5}$ films of 200, 400, 600, 800 and 1000 nm thickness have been studied by X-ray diffraction, the structure of these films are polycrystalline of face center cubic (FCC) structure according to ASTM cards as shown in figure 3, and display strong reflections at (111), (200), (220), (311) and (222) planes, this result in agreement with Elshafie *et al* [3] and Al-Fawade [7].

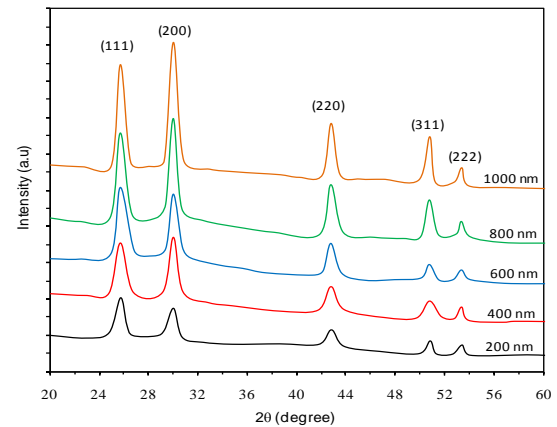


Fig.(1): The X-ray diffraction spectra of thin $Pb_{0.5}S_{0.5}$ films with different thickness.

In all cases, it can be observed that the preferred orientation growth along the (200), it is also observed that the intensity of the peaks increases with increasing the thickness. This can be related to the increasing the concentration by increases the thickness, for this, the grain size increases. The grain size dimensions (D) is calculated from Debye Scherer relation [11]:

$$D = k\lambda / \beta \cos \theta \dots\dots\dots (1)$$

Where k is the shape factor, which is approximately 0.9 and β is the line broadening of pure diffraction profile on 2θ in radius and equal to the full width at half maximum intensity (FWHM) of the peak. However, the increasing of thickness produces an increase in the grain size of $Pb_{0.5}S_{0.5}$ thin films, approximately from 35-59 nm for the thickness (200, 400, 600, 800, 1000) nm respectively, and this agree with Elshafie *et al* [3]. These results are shown in Table (1).

The lattice constant (a) of the films are approximately 5.89Å, and it is increases slightly with thickness. This lattice constant value is very similar to the bulk PbS indicating that films grow on the glass substrate without stresses at the interface. The spacing d values are nearly to that of ASTM cards. Which is 2.969Å and slightly increased has been observed by increased the thicknesses. The micro strain (S), dislocation density (δ) (defined as the length of dislocation lines per unit area) and numbers of crystallites per unit area (N) have been calculated using the following relations [12] and their values are given in the Table (1).

$$S = \beta \cos\theta/4 \dots\dots\dots (2)$$

$$\delta = 1/D^2 \dots\dots\dots (3)$$

$$N = t/D^3 \dots\dots\dots (4)$$

Where t is film thickness. It is interesting to note that the annealing temperature decreases the dislocation density, the number of crystallites per unit area and the strain in the films. The increasing of grain size may increase the surface of area of each grain, which lead to lead to increase of the pores between grains and reduce the pore per unit area on each two adjacent grains, i.e. reduce the strain, then improved relaxed media [3] as shown in Table (2).

Thus the dislocation density decreased and the number of crystallites per unit area increased with increasing the thickness.

Table 1

X-ray diffraction parameters of (200) plane for thin Pb_{0.5}S_{0.5} films at different thicknesses.

t (nm)	D (nm)	a (Å)	d _{exp} (Å)	S × 10 ⁻⁴	δ × 10 ¹⁴ (Lines/m ²)	N × 10 ¹⁵ (m ⁻²)
200	35	5.835	2.917	6.718	8.163	4.665
400	41	5.833	2.911	5.735	5.949	5.804
600	42	5.928	2.959	5.598	5.669	8.098
800	44	5.928	2.963	5.344	5.165	9.391
1000	59	5.948	2.973	3.985	2.873	4.869

Electrical Properties

In order to study conductivity mechanisms, it is convenient to plot logarithm of the conductivity (ln σ/σ₀) as a function of 10³/T for thin Pb_{0.5}S_{0.5} films in temperature range (303–493)K for different thicknesses, as shown in Fig.(2). It is seen that conductivity increased with temperature, indicating semiconducting nature of films. It is clear from these figures that there are two transport mechanisms, giving rise to two activation energies. This result is conforming to Elshafie [3], Al-Fawade [6] and Alias [13]. At higher temperature range (413–493) K, the first activation energy (E_{a1}) occurs, the conduction mechanism here is due to carrier excited into the extended states beyond the mobility edge [14]. While at lower temperature range (303–403) K, the second activation energy (E_{a2}) occurs, the conduction mechanism is due to carrier excited into localized states at the edge of the band [14]. The activation energy

(E_a) can be calculated from the following equation [15]:

$$E_a = (1/K_B T) / \ln(\sigma/\sigma_0) \dots\dots\dots (5)$$

Where σ₀ is the intrinsic conductivity and k_B is Boltzmann constant (8.62 × 10⁻⁵eV/K). Then the activation energy can be calculated from the plot between Ln σ/σ₀ as a function of 10³/T.

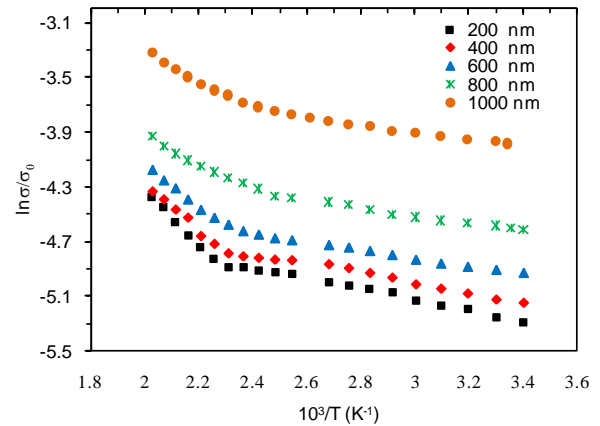


Fig.(2): The behavior of conductivity (Lnσ/σ₀) as a function of temperature (10³/T) of thin Pb_{0.5}S_{0.5} films at different thickness.

Table (2) shows the decreasing of the first activation energy from 0.177 to 0.066 eV and the second activation energy from 0.033-0.00212 as thickness changes from 200 to 1000 nm. These observations may be due to crystallinity improvement of films with increasing thickness. These results are in agreement with Ubale *et al* [16]. The conductivity of the films was determined from the following relation [10]. σ_{d.c} = t/Rwl (6)

Where w is the width of the electrode, ℓ is the distance between the electrodes of the sample, t is the film thickness and R is the sample resistance.

Table (2)

The Variation of activation energies and D.C conductivity of thin Pb_{0.5}S_{0.5} films at different thicknesses.

t (nm)	(413–493)K	(303–403)K	σ _{R.T} × 10 ⁻²
	E _{a1} (eV)	E _{a2} (eV)	(Ωcm) ⁻¹
200	0.1776	0.0330	0.503
400	0.1443	0.0299	0.581
600	0.1029	0.0247	0.725
800	0.0747	0.0236	0.991
1000	0.0686	0.0213	1.859

It is clear that the $\sigma_{R,T}$ increases with increasing of film thickness; this is probably attributed to expected structural discontinuities in thin films. This result is coincident with the results of Ubale *et al* [16], Salim *et al* [17] and Kumar *et al* [18].

From the Hall measurement, Hall coefficient (R_H), carrier concentration (n_H), Hall mobility (μ_H) drift velocity (v_d) can be calculated from the following equations [19]

$$R_H = tV_H / \bar{B}I \dots\dots\dots (7)$$

$$n_H = 1/R_H q \dots\dots\dots (8)$$

$$\mu_H = |R_H| \sigma \dots\dots\dots (9)$$

$$v_d = \mu_H E \dots\dots\dots (10)$$

Where q is the electron charge and E is the electrical field strength. Table (3) illustrates the Hall Effect parameters. All prepared films with different thicknesses have a positive Hall coefficient, which means that the prepared thin $Pb_{0.5}S_{0.5}$ films are p-type semiconductors. The conductivity and the carrier's concentration increases with increasing of thickness, also to notice from Table (3) that mobility and drift velocity decreases with increasing of thickness.

Table 3

The Variation of Hall coefficient, carrier concentration, Hall mobility and drift velocity of $Pb_{0.5}S_{0.5}$ thin films at different thicknesses.

t (nm)	R_H (cm^3/c)	$n_H \times 10^{19}$ (cm^{-3})	$\mu_H \times 10^{-2}$ ($cm^2/V.s$)	$v_d \times 10^{-2}$ (cm/s)
200	0.126	0.079	3.992	39.925
400	0.299	0.187	1.941	19.417
600	0.472	0.295	1.534	15.345
800	10.08	6.299	0.121	1.2169
1000	15.28	9.547	0.098	0.9820

Conclusions

$Pb_{0.5}S_{0.5}$ alloys have been prepared successfully by the method of quenching from elements. The structure of thin $Pb_{0.5}S_{0.5}$ films with different thicknesses is polycrystalline with cubic structure, the grain size increases as film thickness increase. The electrical conductivity increases as film thickness increase and therefore activation energy are observed to be thickness dependent. The Hall effect measurements confirm the p-type nature of thin $Pb_{0.5}S_{0.5}$ films. Also the charge carrier concentration increases with increasing

thickness, whereas, the Hall mobility and drift velocity decreased with increasing of film thickness.

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٣٥ الى ٥٩ نانومتر. سجلت التوصيلية المستمرة مرحلتين للتوصيلية خلال كل المدى الحراري. تزداد قيمة التوصيلية المستمرة من ١٠×١٠^{-١٠} الى ١٠×١٠^{-١٠} (أوم.سنتيمتر)^{-١} بزيادة سمك الأفلام. جميع الأفلام المحضرة لها قيمتان لطاقتان التنشيط، حيث تتناقص القيم بزيادة السمك. كانت أعلى قيمة لطاقة التنشيط هي ٠,١٧٧ إلكترون فولت عند سمك ٢٠٠ نانو متر، ثم تتناقص الى ٠,٠٦٧ إلكترون فولت عند المدى الحراري ٤٩٣–٤١٣ درجة مطلقاً. بينت نتائج تأثير هول أن جميع الأغشية $Pb_{0.5}S_{0.5}$ المحضرة هي مواد من النوع المانع. يزداد تركيز الحوامل بزيادة السمك، وتتغير قيمته من $١٩١٠ \times ٠,٠٧٩$ الى $١٩١٠ \times ٩,٥٥$ (سنتيمتر)^{-٣} للأسمك من ٢٠٠–١٠٠٠ نانو متر. تتناقص تحريكه هول من ٣,٩٩–٠,٠٩٨ (سنتيمتر^٢/فولت.ثانية) بزيادة السمك من ٢٠٠–١٠٠٠ نانو متر. تتناقص سرعة الانجراف بزيادة سمك هذه الأفلام.

الخلاصة

حضرت سبيكة $Pb_{0.5}S_{0.5}$ بنجاح بطريقة التبريد السريع لصهارة العناصر. حضرت أغشية $Pb_{0.5}S_{0.5}$ الرقيقة بأسمك ٢٠٠, ٤٠٠, ٦٠٠, ٨٠٠ و ١٠٠٠ نانومتر من السبيكة المحضرة بتقنية التبخير الحراري على أرضيات زجاجية عند درجة حرارة الغرفة. بينت دراسة حيود الأشعة السينية أن الأفلام المحضرة هي بتركيب مكعبي متعدد التبلور مع قمم عالية عند السطوح (١١١) و (٢٠٠)، تزداد شدة القمم بزيادة السمك. يزداد الحجم الحبيبي بزيادة السمك و تتغير قيمته بين