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The effect of Pb content and annealing temperature on the electrical properties of Pb_xS_{1-x} films

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Abstract

A polycrystalline lead sulfide Pb_xS_{1-x} alloys with various Pb content (x=0.50, 0.51, 0.52, 0.54, and 0.55) has been prepared successfully. Pb_xS_{1-x} films of thickness 1.5μm have been deposited onto glass and n-Si substrates by flash thermal evaporation method at room temperature (R.T) under vacuum 10^{-6} torr and deposition rate $0.83x10^{-3}$μm/sec. These films have been annealed at different temperatures ($T_{a=}$R.T, 323, 373, 423, 473, and 523) K. The electrical properties of these films were studied by variation of Pb content and annealing temperature. The d.c conductivity increases with increasing Pb content for all Pb_xS_{1-x} films and decreases with increasing T_a. The electrical activation energy increases at range of temperatures and decreases in other range of temperatures with increasing annealing temperature and Pb content. From the Hall Effect measurement, the films of (x=0.50, 0.51, and 0.52) are found p-type and the films of compositions (x=0.54 and 0.55) are n-type and change to p-type at 523K. The carriers concentration decreases with increasing annealing temperatures and Pb content for p-type, while it increases with increasing annealing temperatures and decreases with increasing the Pb content for n-type samples. The Hall mobility increases sharply with increasing T_a and Pb content for p-type films, while it increases with increasing Pb content and decreases with increasing T_a for n-type films. The drift velocity (v_d), carrier life time (τ), and mean free path (l) increase with increasing annealing temperatures for p-type and decreases for n-type, while it increases with increasing Pb content for both p-type and n-type films. From measurements of the four points probe method, it is found that the silicon is of n-type, whereas Pb_xS_{1-x} are p- type for (x=0.50, 0.51 and 0.52) and n-type for (x=0.54 and 0.55).

Keywords: Pb_xS_{1-x} films; Electrical conductivity; Hall mobility.
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1. Introduction

Lead sulfide (PbS) is a polar semiconductor which has a nature of chemical binding of mixed ionic-covalent bonds where in a purely ionic compound the Pb^{+2} ion has three vacant p states, while the S^{-2} ion has one pair of electron in (s-state) and three pairs of

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electrons in the p-state, each sulfur ion is surrounded octahedral by six lead ions and similarly, a lead ion is surrounded by six sulfur ions [1].

The PbS thin films can be used as a photoconductive and photovoltaic detector, and this material is among the earliest that has been used as high-performance photoconductive detectors and are still widely used because of their good performance and cheep fabrication method as well as its operation in the range 0.7-3μm [2] . The electrical properties measurements of semiconductor thin films allow the 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, however, depend upon the nature of semiconductor if they are pure or doped, crystalline or amorphous [3].

The electrical conductivity (σ) is defined as the proportional factor between the current density J and the electric field E, and it is given by the equation:

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

where $\sigma=ne\mu$ or equals to $ne^2\tau/m^*$ and J is current density. In semiconductors the relation between the current density and electric field (E) is given by [4]:

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

where n and p are the electron and hole concentrations μ_e and μ_h are the electron and hole mobility respectively and q is the electron charge , where μ is equal to V_d/E and V_d is drift velocity. The relation between the conductivity and the electron-hole concentration is[4,5]:

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

For most cases of semiconductor the following equation gives the variation of the electrical conductivity with temperature:

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

Where σ_o is the minimum electrical conductivity at (0)K, E_a is the activation energy which is corresponding to the ($E_g/2$) for intrinsic conduction [6,7] and k_B is the Boltzmann constant.

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 (B) and the current and called Hall voltage [8],as shown in Fig.(1). This is known as the Hall Effect and it is widely used to distinguish between the type of the carriers, the concentration and to determine the carriers mobility in the materials.

The Hall coefficient (R_H) is found by

$$R_H=\pm1/nq \quad (5)$$

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 [9]:

$$R_H=t\, V_H/IB \quad (6)$$

Where t is the sample's thickness. If the conduction is due to the one carriers type (e.g.: electrons) then we can find the mobility from the equation [10]:

$$\mu=\sigma\ /n\, q \quad (7)$$

or

$$\mu=\sigma R_H \quad (8)$$

Jensen and Schoolar (1976)[11] have measured the Hall coefficient and mobility at 77and 300K of n- and p-type of PbS_xSe_{1-x} epitaxial films on (111) BaF_2 as a function of the thickness. They used over coating of As_2S_3 with thickness 0.3 μm. The maximum mobility is found $4x10^5 cm^2/V.sec$ and R_H is about $2cm^3/C$. Elabd & Steckl(1978) [12] have grown PbS thin films on glass, gold-on-glass, and Si substrate by chemical deposition at room temperature. Using Hall effect, they found that the resistance R = ($1\text{-}2\times10^5$) ohm, ρ = 5(ohm.cm), and $\mu_H=225cm^2/V.sec$. They also annealed the films at temperature (373 and 573) K and observed an increase in resistivity. George et al (1986) [13] have studied the effect of substrate temperature at (300,400,560) K and T_a in range (100-400) K on the PbS films prepared by reactive evaporation. They found that films are amorphous in nature at RT substrates, but increasing substrate temperature made the films polycrystalline. Hall Effect measurements showed that the films are p-type and have carriers concentration of 6×10^{17} cm^{-3}. They also found that mobility, and carrier concentration increase with increasing temperature. They also found that conductivity decreases with T_a and the films have high thermoelectric power. Chu et al (1987) [14] have fabricated PbS and PbSe as a heterostructure. The samples are grown on BaF_2 (111) substrate by a hot wall technique at substrate temperature of 623K. Carrier density are $3x10^{17}$ cm^{-3}. The room temperature mobility is $500cm^2/V.sec$ and $1000cm^2/V.sec$ for PbS and PbSe and 15000 and 25000 $cm^2/V.sec$ for PbS and PbSe at 77K. They also found from spectral response study at 77K that there are two peaks one of them for PbS (0.307) eV and the other for PbSe (0.176) eV, while E_g for PbS and PbSe at 273K are 0.41eV and 0.27eV respectively. The activation energy was reported 0.048 ±0.003eV. The electrical properties of these films are very important for designing the energy band diagram of PbS heterojunctiom detectors and fabricating this junction is of a high demand for many applications in various industrial field especially in photonic technology.

The aim of this work is, therefore, to prepare Pb_xS_{1-x} as a bulk and films by flash thermal evaporation technique. The effects of x content and annealing temperature on the electrical properties of Pb_xS_{1-x} films have been studied.

2. Experimental

The Pb_xS_{1-x} films of (1.5) μm thickness have been prepared by vacuum flash evaporation technique using Edward E306A under lower pressure of about 10^{-6}mbar. By the flash evaporation techniques, the weighting of the required amount of material placed into molybdenum boat. To have high sensitive layers, various heat treatments have been used in vacuum by electric furnace in the range (RT-523) K. Then the samples are ready for testing by the following measurements. The electrical measurements are included the D.C conductivity and Hall Effect for samples deposited on glass substrate with Al electrodes of thickness 200 nm. The type of conductivity and resistivity can be known from four points probe method.

The electrical resistance has been measured as a function of the temperature for Pb_xS_{1-x} films of thickness (1.5) μm at different values of x content and T_a. The measurements have been performed using a sensitive electrometer type of (Keithly Digital Electrometer (616) and vacuum electric oven. The resistivity and conductivity as a function of T and the value of the activation energy is calculated from a computer program.

The Hall effect has been measured using an electrical circuit which contain (D.C power supply (0-40) V. When the samples carrying a current and exposed to a constant magnetic field(B=0.254T) perpendicular to the electric field then an e.m.f is called Hall voltage(V_H) is set up across the sample, then the I and V_H were recorded by using Keithley digital electrometer. The type, concentration and mobility of the carriers for Pb_xS_{1-x} films at different value of x content and T_a can be calculated by equations (5), (6), and (8).

The Four points probe method of type (FPP500) have been used for exploring the resistivity and the type of conductivity for silicon wafers and Pb_xS_{1-x} films at different values of x content and T_a . When the samples are placed in contact with the four probes, a small current is passing between the external points and the voltage is measured between the internal points. The surface resistance (R_S) and the resistivity can be represented by the following relation [15, 16]:

$$R_S=V/I\ (C.F)\ \Omega \tag{9}$$

where (C.F) is the correction factor and equal to (4.54)[17], the resistivity may then be calculated:

$$\rho= R_S\ t(\Omega.cm) \tag{10}$$

Finally the type of the junction (isotype or anisotype) can be determined.

3. Results and Discussion

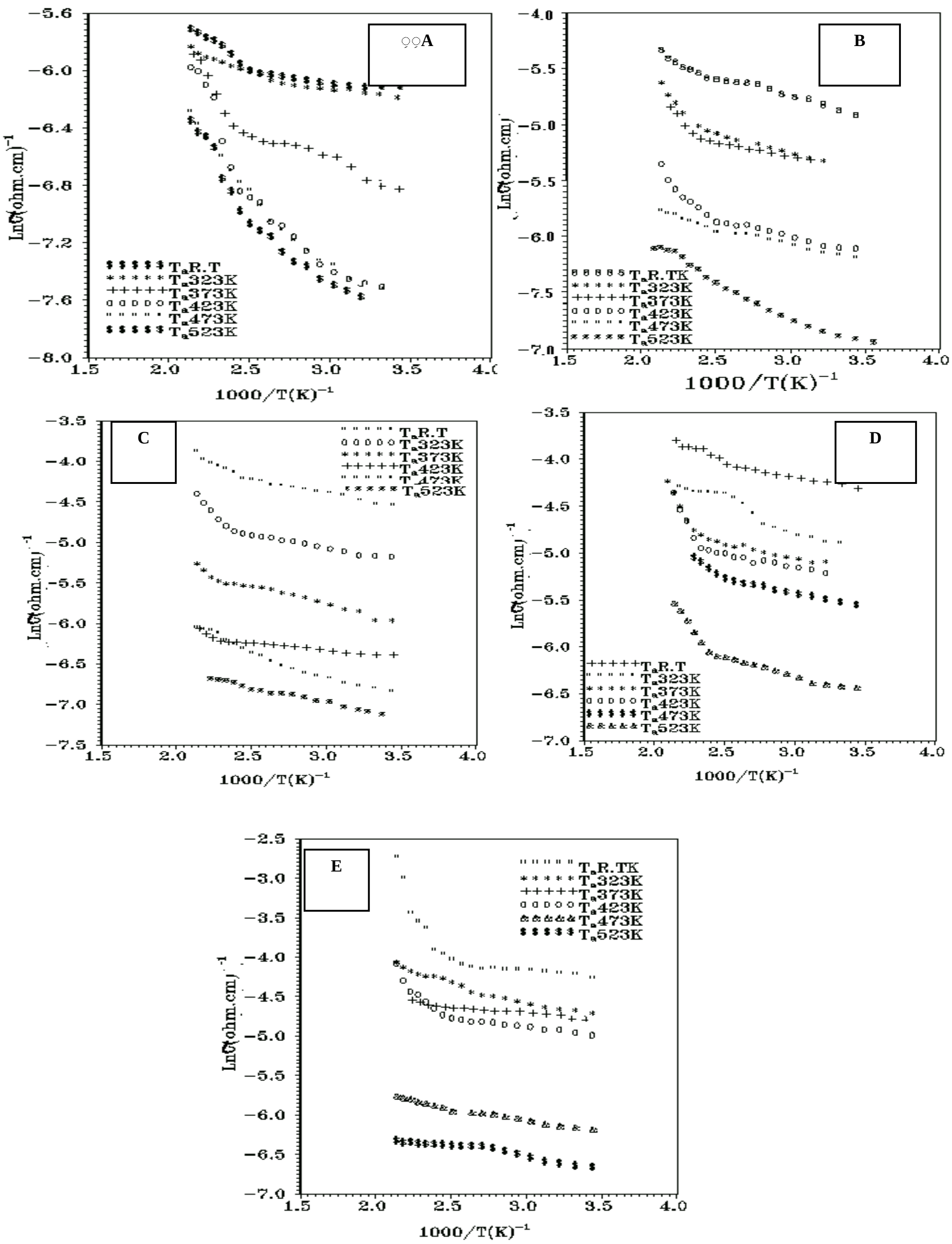


Fig.(1) The plots of lnσ versus $10^3/T$ for Pb_xS_{1-x} at different T_a and x content.

The plots of lnσ versus $10^3/T$ for Pb_xS_{1-x} at RT and different annealing temperatures (323, 373, 423, 473 and 523) K and Pb content (0.50, 0.51, 0.52, 0.54 and 0.55) are shown in figures (1a-e). In general, it can be observed from these figures that the D.C conductivity increases with increasing Pb content and the behavior is not linear with temperature. This increase means a negative coefficient of resistance while the conductivity decreases with increasing annealing temperatures. Also, two mechanisms can be seen for some samples and one for others from which the values of the activation energies (E_{a1}) and (E_{a2}) are calculated. The variation of conductivity at room temperatures ($\sigma_{R.T}$) as a function of annealing temperatures is presenting in Fig. (2). The $\sigma_{R.T}$ is found to decrease with increasing annealing temperatures from R.T to 523K and for $Pb_{0.5}S_{0.5}$ film it decreases about four times of magnitude for un annealed films at R.T to annealed films at 523K (0.214×10^{-2}-0.51×10^{-3} $(\Omega.cm)^{-1}$).Whereas for $Pb_{0.51}S_{0.49}$ films, $\sigma_{R.T}$ decreases about eight times of magnitude (0.72×10^{-2}-0.95×10^{-3} $(ohm.cm)^{-1}$) and about ten times of magnitude for others alloys. The decreases in the $\sigma_{R.T}$ with increasing annealing temperatures is attributed to a decrease in the defect states which leads to an increase in the mobility and energy gaps and this is in agreement with George et al findings[13].

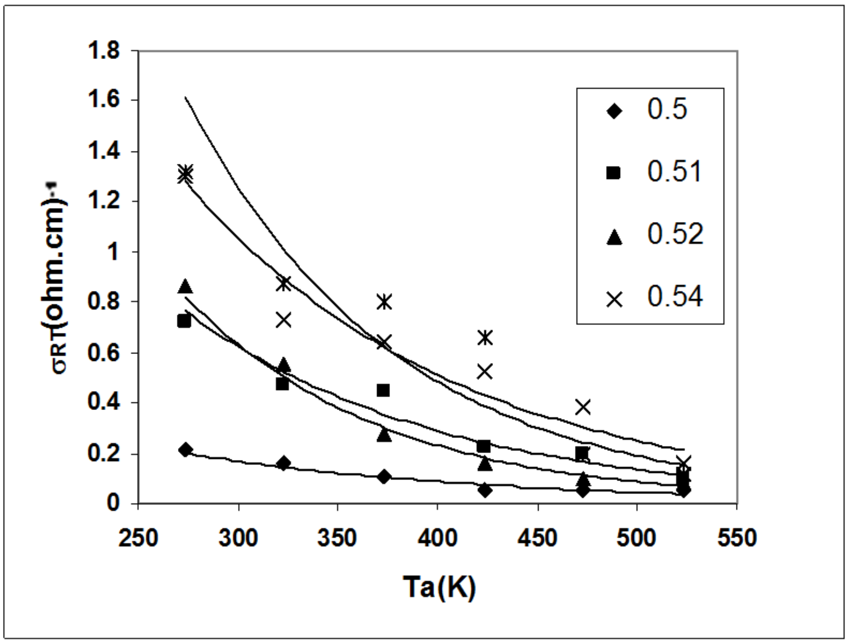


Fig. 2: The variation of $\sigma_{R.T}$ for Pb_xS_{1-x} films at different Pb content and T_a..

Figure (3) shows the effect of annealing temperature on the activation energies E_{a1} and E_{a2} for Pb_xS_{1-x} films. It is clear that some samples have one activation energy and two for the others and the values of E_{a1} and E_{a2} increase for some sample and decreases for others with increasing T_a . For $Pb_{0.5}S_{0.5}$ films, the value of E_{a1} changes from (0.07-0.116) eV while the value of E_{a2} changes from 0.0113 to 0.063eV for annealing temperatures from R.T to523K whereas for $Pb_{0.51}S_{0.49}$ film the value of E_{a1} changes from 0.0656 to 0.17eV and decreasing at 473K to 0.043eV then decreases to 0.06eV and the value of E_{a2} is nearly constant at the same value. For $Pb_{0.52}S_{0.48}$ the value of E_{a1} increases from 0.008 to 0.15eV and decreases after that for the other values and the value of E_{a2} decreases from 0.028 to 0.0154eV for $Pb_{0.54}S_{0.46}$ film the value of E_{a1} increases from 0.021 to 0.184eV whereas the value of E_{a2} increases from 0.031 to 0.024eV and then increases to 0.032 at 423K but it decreases and decreases from 0.016 to 0.023eV for 473K and 523K respectively. The value of E_{a1} for $Pb_{0.55}S_{0.45}$ films varies between (0.034-0.023) eV, and the value of E_{a2} decreasing from 0.023 to 0.019eVfor T_a from R.T to 423K and then increased to 0.023eV at 523K. The increasing of E_{a1} and E_{a2} is attributed to improvement in structure while the decrease is due to creating localized states by annealing and this temperature is not enough to improve or varying in the structure of these films.

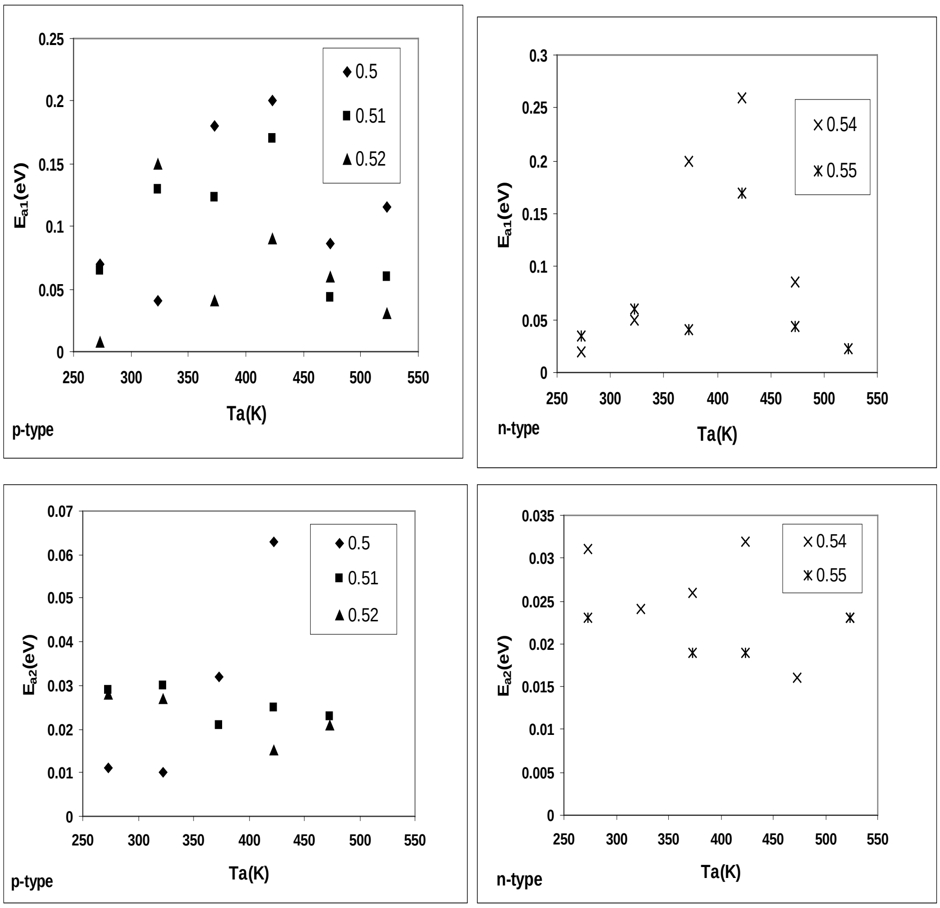


Fig. 3: The variation of E_{a1} and E_{a2} for Pb_xS_{1-x} films at different Pb content and T_a.

The $\sigma_{R.T}$ increases about three and half times by increasing x from (0.50 to 0.51) and four times at 0.52 value, six times for x= 0.54 value and six and half times for x= 0.55 value (Fig .2). This may be due to a change in the localized states, structure and composition of films as well as to the rearrangement of atoms which yields fewer defects. While the behavior of E_{a1} and E_{a2} is not linear with increasing of Pb content .The increase in Pb content leads to a decrease in activation energy leading to saturation in the dangling bonds. There is also a reduction in the density of states occurs at Fermi level which caused a transfer from conductivity near the Fermi level to the thermal activation conductivity at the band gap.

From the Hall measurements, the type, concentration(n_H), mobility(μ), drift velocity (v_d), lifetime (τ) and mean free path (l) of the carriers have been calculated according to equations 1-8 for Pb_xS_{1-x} the films at different Pb content and annealing temperatures. It is observed from Fig. (4) that the films of (x=0.5, 0.51 and0.52) are p-type and the films of (x=0.54 and 0.55) are n-type and this attributed to exposure to air or by heat treatment as well as the presence of excess sulfur vapor which may produce vacant PbS sites that form shallow acceptor levels and will not leave any unreacted lead inside the grains during the deposition and annealing films.

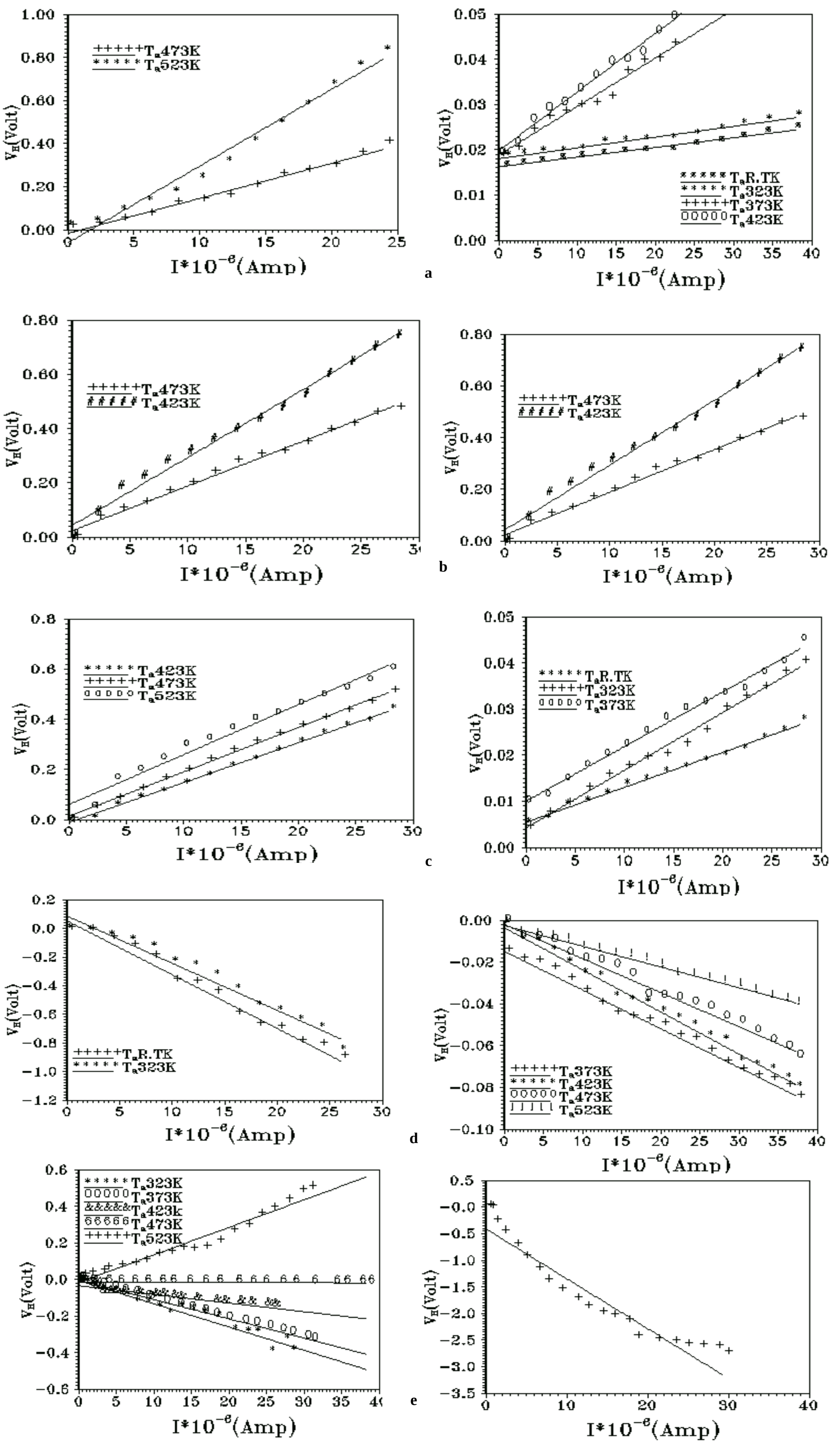
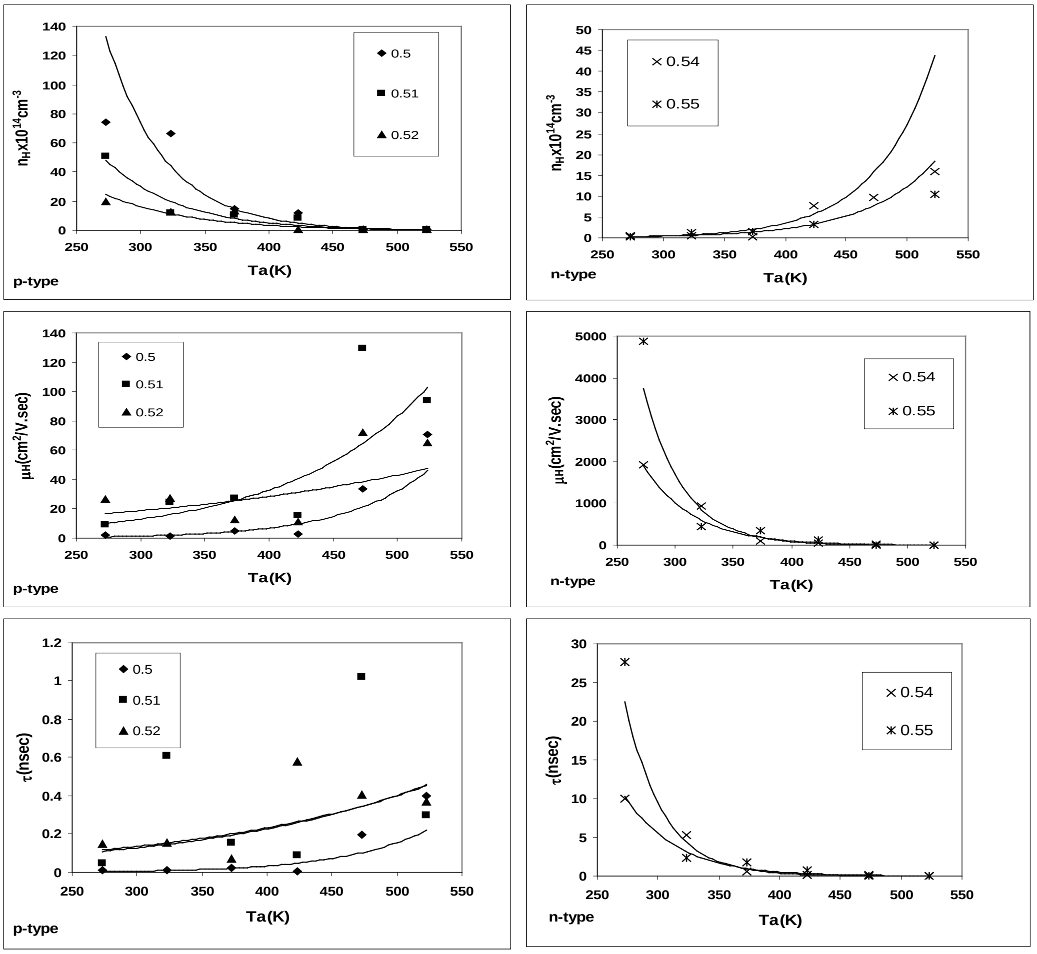


Fig (4) Hall voltage as a function of current for Pb_xS_{1-x} films at different T_a and Pb content of a-0.50 ,b-0.51, c-0.52, d-0.54, e-0.55.

While the films of x=0.54 and 0.55 are n-type and changes to p-type when annealed at T_a=523K because the excess in Pb acts as donor atoms and at this annealing temperature there is an excess in S atoms by annealing [18] .The variation of carriers concentration and the Hall mobility with T_a of Pb_xS_{1-x} films at different Pb content and annealing temperatures are shown in Figs.(5a&b) . It is noticed from these figures that the carrier's concentration decreases with increasing annealing temperatures and Pb content for p-type while it increases with increasing
annealing temperatures and decreases with increasing Pb content for n-type samples. Also it can be observed from Fig.(5) that the mobility increases sharply with increasing T_a and Pb content for p-type whereas it decreases with increasing T_a and increases with increases Pb content for n-type. The explanation of increasing in mobility with T_a for p-type is due to reduction of the scattering of the carriers from the surface as well as the elimination of the defects in the films(as it is seen from the X-ray study[19]) and the increasing in crystallite size that decreasing the number of grain boundaries.

From the Hall mobility measurement, τ, v_d and l of the carriers have been calculated by the equations(1) and (2) for Pb_xS_{1-x} films at different Pb content and annealing temperatures, and the results are shown in Fig. (5). All these parameters are increased with increasing annealing temperatures and Pb content for p-type while it decrease with increasing annealing temperature and increase with increasing Pb content for n-type. The reason for this variation was mentioned above.



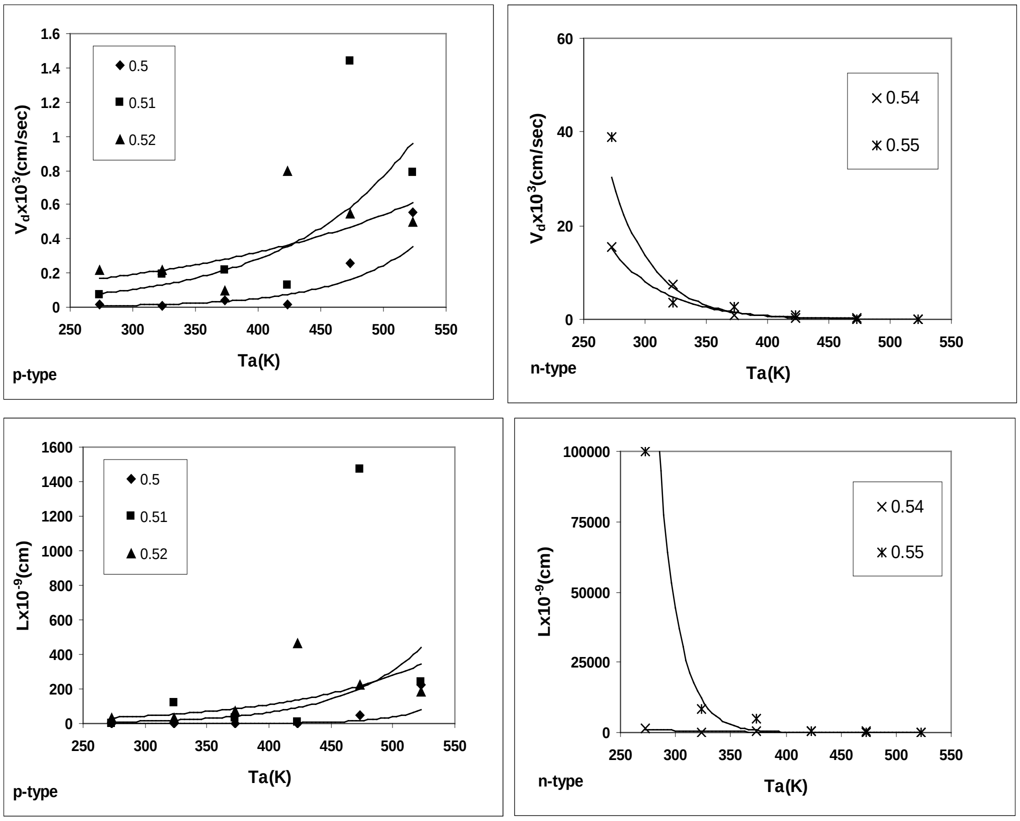


Fig.(5) The variation of carriers concentration, Hall mobility, lifetime, Drift velocity and mean free path for Pb_xS_{1-x} films at different Pb content and annealing temperatures.

The surface resistance is a very important parameter which indicates the type of the junction whether it is abrupt or not and also the type of the substrate. The silicon is n-type whereas the Pb_xS_{1-x} with different x contents are p- type for x = (0.5, 0.51 and 0.52) and n-type for (0.54 and0.55) and this in a qualitative agreement with the result of the Hall measurements. So that annealing of sulfur vapor at 873K transform the n-type to p-type and to fabricate the p-n heterojunction (HJ). It is observed that the surface resistance of the samples are increased by increasing the x content as shown in Table(1) due to increase the defects and localized states through increasing the Pb content and due to the high lattice mismatch and thermal expansion coefficient. That affects the electrical conductivity leading to increase the surface electrical resistance. Also the surface resistance decreases with increasing annealing temperatures which mean that the defects and dislocations at the surface decreases with increasing T_a and this is in agreement with Mohammed[20-22] who found that the surface resistance was equals to 3440 ohm/square and equals to 1544 ohm/square after annealing for PbS/n-Si HJ. This value of the surface resistance will affect the value of the resistivity and conductivity calculated by equations (9&10) as shown in Table (1), in which the conductivity increases with increasing T_a and decreases with increases Pb content.

Table (1) The variation of surface resistance with T_a and Pb content.

x	surface Resistance Ω/cm^{2}				
	T_a(K)				
	RT	373	423	473	423
0.50	303.1	211	176.3	97	88
0.51	1315	950	820	312	200
0.52	2425	2133	1025	400	350
0.54	3999	2488	1089	900	820
0.55	5653	3999	3950	2000	1271.2
	ρ_S (ohm.cm)				
0.50	0.05	0.03	0.02	0.015	0.013
0.51	0.19	0.14	0.12	0.047	0.030
0.52	0.37	0.32	0.15	0.060	0.053
0.54	0.59	0.37	0.16	0.155	0.123
0.55	0.85	0.59	0.55	0.300	0.190
	σ_S (ohm.cm)$^{-1}$				
0.50	22	31	50	66.7	76.9
0.51	5.3	7.1	8.1	21.3	33.3
0.52	27	3.1	6.7	16.7	18.9
0.54	1.7	2.7	6.3	6.45	8.13
0.55	1.2	1.7	1.8	3.3	5.3

4. Conclusions

The electrical properties of these films are very important for fabrication photoconductive and photovoltaic detectors and for designing the model of an energy band diagram . From the data of the present work, it is concluded that:

- The Pb_xS_{1-x} alloys for (x = 0.50, 0.51, 0.52, 0.54and 0.55) have successfully prepared, as bulks and films at different conditions.
- The mechanism of conductivity occurs in two ranges of temperature for some samples and one mechanism for others.
- The d.c conductivity increases with increasing the Pb content for all Pb_xS_{1-x} films, while it decreases with increasing T_a.
- The electrical activation energy increases at a range of temperatures (RT-523K) and decreases in other range of temperatures with increasing annealing temperature and Pb content.
- The Hall measurement shows that the films of x=0.50, 0.51 and 0.52 are p-type and the films of x=0.54 and0.55 are n-type and change to p-type at 523K.
- The carriers concentration decreases with increasing annealing temperatures and Pb content for p-type while it increases with increasing annealing temperatures and decreases with increasing Pb content for n-type samples.
- The Hall mobility increases sharply with increasing T_a and Pb content for p-type, while it increases with increasing Pb content and decreases with increasing T_a for n-type.

- The drift velocity, carrier life time, and free mean path increase with increasing annealing temperatures for p-type and it decreases with increasing T_a for n-type and it increases with increases Pb content for p-type and it decreases with increasing Pb content for n-type.
- From measurement of the four points probe method, it is found that silicon is n-type whereas the $PbxS1_{-x}$ are p- type for x= (0.50, 0.51and 0.52) and n-type for x= 0.54 and 0.55.

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