Some electrical properties of thin PbS films

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Abstract

An alloy of PbS has been prepared in an evacuated quartz tube (Pb: S = 50:50). The structure of the ingot examined by X-ray diffraction and found to be polycrystalline of cubic phase structure with dominate orientation at (200) plane. The PbS thin films have been deposited by thermal evaporation technique under pressure 5×10^{-5} mbar with thickness of about 0.5 μm. These films have been annealed at different temperature (T_a) (373, 423, 473 and 523 K˚) under vacuum. The electrical measurements showed that the d.c. conductivity ($\sigma_{d.c.}$) decreased with increasing T_a, while the activation energy increased with increasing T_a. The Hall effect measurements prove that the films are P-type and the carriers concentration (n_H) decreased with increasing T_a. Hall mobility (μ_H), drift velocity (υ_d), carriers life time (τ) and mean free path (ι) have increased with increasing T_a. The thermoelectric power experiment confirmed the Hall Effect measurements. Seebeck coefficient (s), thermal activation energies (E_s) and Energy of hopping (ΔW) for PbS films have increased with increasing T_a.

الخلاصة

تم تحضير سبيكة كبريتيد الرصاص داخل أنبوبة كوارتز مفرغة (Pb:S=٥٠:٥٠)، تم فحص التركيب البلوري للسبيكة بحيود الأشعة السينية، حيث وجد أن تركيب السبيكة متعدد التبلور بالطور المكعب والاتجاه البلوري المسيطر هو (٢٠٠).تم تبخير مركب كبريتيد الرصاص بتقنية التبخير الحراري تحت ضغط ٥ □١٠-٥ملي بار، بسمك ٠,٥ مايكرونات، ثم تم تلدين هذه الأغشية بالفراغ بدرجات تلدين مختلفة (٣٧٣، ٤٢٣، ٤٧٣ و ٥٢٣) مطلقة.القياسات الكهربائية أظهرت بان التوصيلية المستمرة للأغشية تتناقص بزيادة حرارة التلدين، في حين تزداد طاقة التنشيط بزيادة حرارة التلدين.

1. Introduction

Lead Sulfide is a direct narrow gap semiconductor, at room temperature, its energy band gap approximately 0.37-0.4 eV[1, 2], which has cubic lattice with unite cell face center cube [3]. Lead sulfide have many optical characteristics in comparison with other semiconductors, the band gap are smaller at lower temperature, i.e. the temperature coefficient of energy gap are positive, while it is negative for other elements and compounds semiconductor, the lattice structure may be very unstoichiometric and the static dielectric constants of PbS are much larger than those of Si, GaAs and other semiconductors [4]. PbS is very suitable for infrared detection application, photoresistance, diode laser, humidity and temperature sensors, decorative coating and solar control coatings [5]. For these reasons, many researches groups have an increasing interesting in the development and study of this material. It's well known that the chemical bath deposition technique (CBD) is the most convenient and frequently used deposition technique to grow PbS thin films. It has been found that the properties of chemical deposition PbS films depends strongly on the growth conditions. In fact, the optical characterization of polycrystalline films can used to obtain structural and morphological information from these materials [5].

2. Experimental

At first an alloy of pbS compound has been prepared by mixing Pb and S elements (by mayer comp.) with purity of about 99.999%, in an evacuated quartz tube and heating in computerized furnace according to the phase diagram of PbS and then the resulting alloy was quenching. The ratio of Pb:S is 50:50. Next, a thin PbS films were deposited on glass substrate by thermal evaporation technique using Blazers unite model (BAE 370) with controlled thickness equal to 0.5 µm under vacuum of about 5×10^{-5} mbar. A high purity layer of aluminum was deposited on PbS thin films as terminal contacts. And then the specimens were treated under different annealing temperature between 373 - 523 K under vacuum of about 30 mbar by Memert evacuated oven. Finally, XRD technique was used to calculate some structural parameters for the prepared alloy such as, crystal inter atomic spacing, the relative intensities of peaks and Bragg diffraction angle (2θ). The XRD patterns were obtained using a diffractometer CuK_α radiation (λ=1.54056 Å) in the 2θ scanning mode. Some

electrical properties of thin PbS films like d.c. conductivity, Hall measurements and thermoelectric power were measured for different annealing temperatures.

3. Results and Discussion

The X-ray diffraction pattern of PbS alloy has been studied and its shown in figure (1). The X-ray diffraction spectrum shows a polycrystalline structure and display five diffraction peaks at 2θ values of approximately 25.4, 29.5, 42.5, 50.4 and 52.9□ which correspond to (111), (200), (220), (311) and (222) planes of PbS cubic phase respectively. Its observed a preferred orientation grows along (200) direction. This result in good agreement with Valenzuela *et al*[5] and Ubale *et al*[6]. The X-ray diffraction parameters are tabulated in table (1)

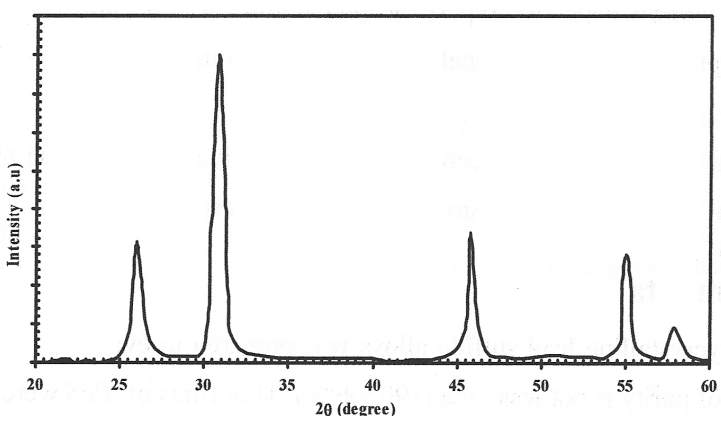


Fig.(1) the X-ray diffraction spectrum of PbS alloy

Table (1) X-ray diffraction parameters of PbS alloy

hkl	I/I□ stnd.	$d_{stnd.}$(Å)	2θ(degree)	$d_{exp.}$ (Å)
111	84	3.429	25.4	3.503
200	100	2.696	29.5	3.025
220	57	2.099	42.5	2.127
311	35	1.790	50.4	1.810
222	16	1.714	52.9	1.731

4. d.c. conductivity:

The dark conductivity of PbS films was studied in the range of 290- 500 K using temperature gradient method. Fig.(2) shows the variation of Ln of the conductivity (Ln σ) with reciprocal temperature (1000/T) for different annealing temperature T_a.. Its found that the behavior of electrical conductivity is not linear and decreases with increasing temperature this means a negative coefficient of resistance [7].

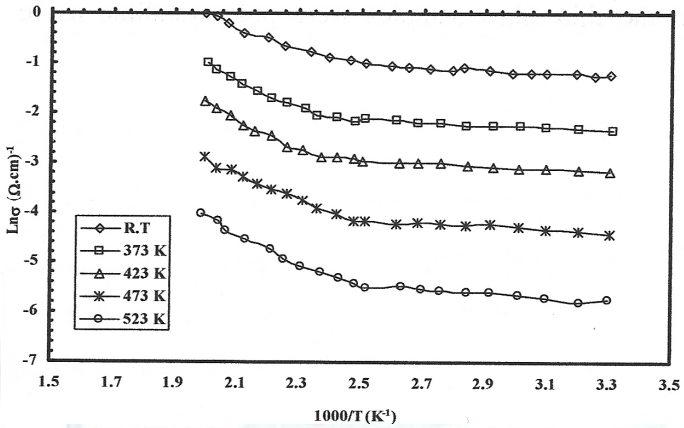


Fig.(2) The variation of Ln σ vs 1000/T for PbS thin films.

Also it can be observed that there are two regions of conductivity throughout the heating temperature range where the first one (E_{a1}) occurs at higher temperature within the range (393 -503)K˚ and the second activation energy(E_{a2}) occurs at lower temperature within the range (293 -393)K˚, E_a can be found by taking the slope of straight line for the curves in figure 2.

It may be seen that the conductivity decreases with increasing the annealing temperature for all films at different T_a as shown in figure 3, this decrease might be due to decrease in the defect state which leads to increase in the mobility and energy gap , this is in good agreement with George [8].

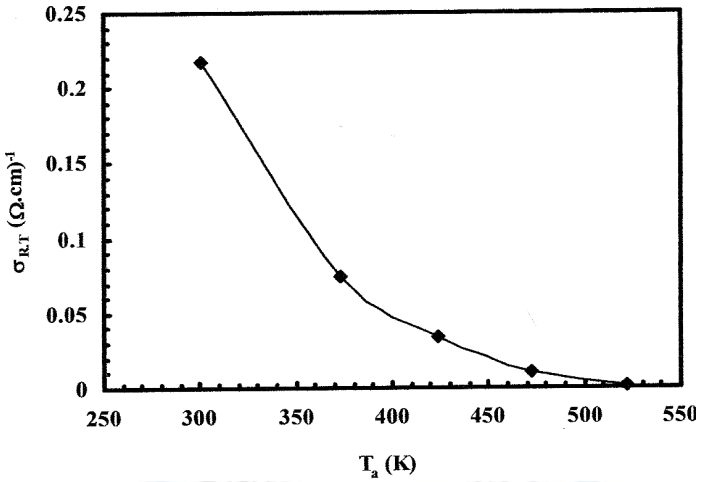


Fig.(3) The variation of σ_{RT} vs T_a for PbS thin films.

The two values of activation energies (E_{a1} and E_{a2}) increase with increasing the annealing temperature as shown in figure 4.this change in activation energies may refer to the structural improvement due to eliminate defect through annealing [9]. Our results are good agreement with Levechenko *et al* [9] and al-Fawade [10].

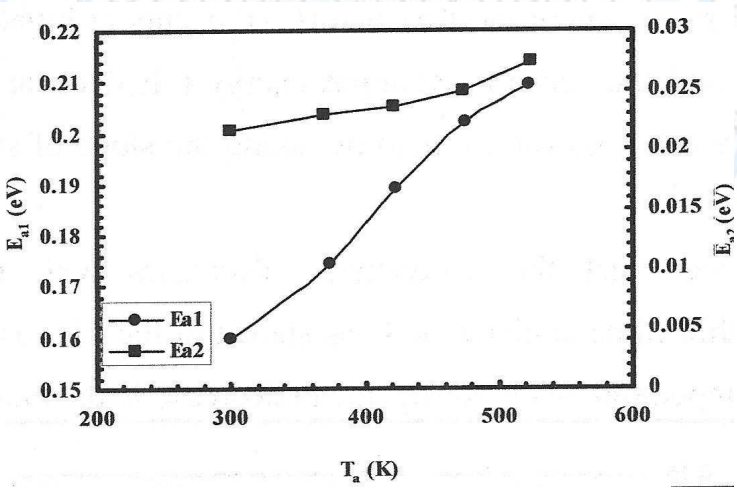


Fig.(4) The variation of E_{a1} and E_{a2} vs T_a for PbS thin films.

5. Hall effect

The variation of Hall voltage (V_H) with the current for polycrystalline thin PbS films at room temperature and heat treated shown in figure 5. the lattice structure may be

unstochiometric, and the interstitials control the conductivity type. The prepared thin PbS films are p-type due to the vacancies of sulfide ion [2], that means the conduction is dominated by holes and this agreement with Ubale *et al* [6], Levechenko *et al* [9] and al-Fawade [10].

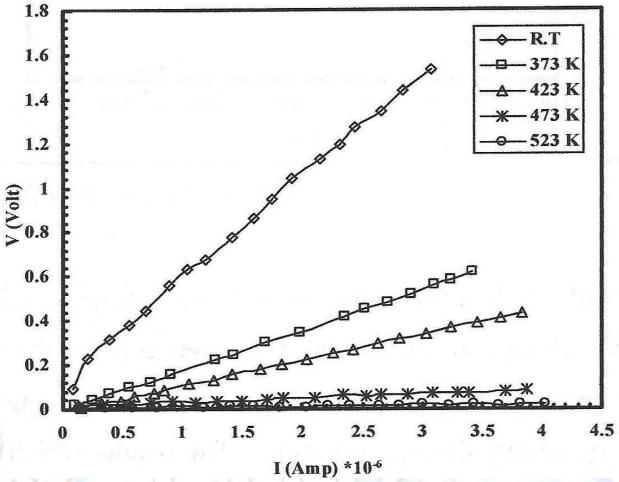


Fig.(5) The variation of Hall voltage (V_H) with the current for PbS thin films.

The variation of carrier concentration (n_H) and Hall mobility (μ_H) with annealing temperature for thin PbS films are shown in figure (6). It was found that the carriers concentration decrease with increasing the annealing temperature while Hall mobility increases with increasing the annealing temperature. This behavior is due to existence of the potential barrier in the grain boundaries and this agreement with Woods [11], reports that μ_H of PbS thin films for 0.5 μm thick equel to 4.7 cm^2 /V.S.

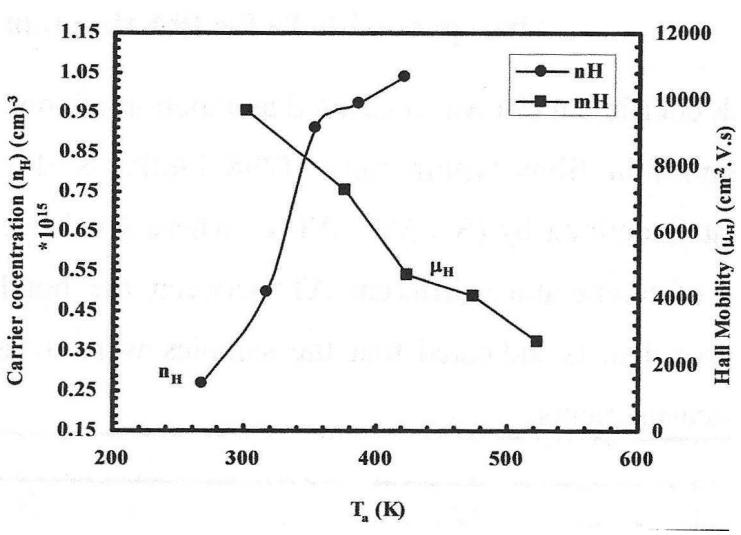


Fig.(6) The variation of carrier concentration (n_H) and Hall mobility (μ_H) with annealing temperature for thin PbS films

From Hall mobility measurements, the drift velocity (V_d), carrier life time (τ) and mean free path (ι) are found to increase with increasing the annealing temperatures and shown in fig. (7).

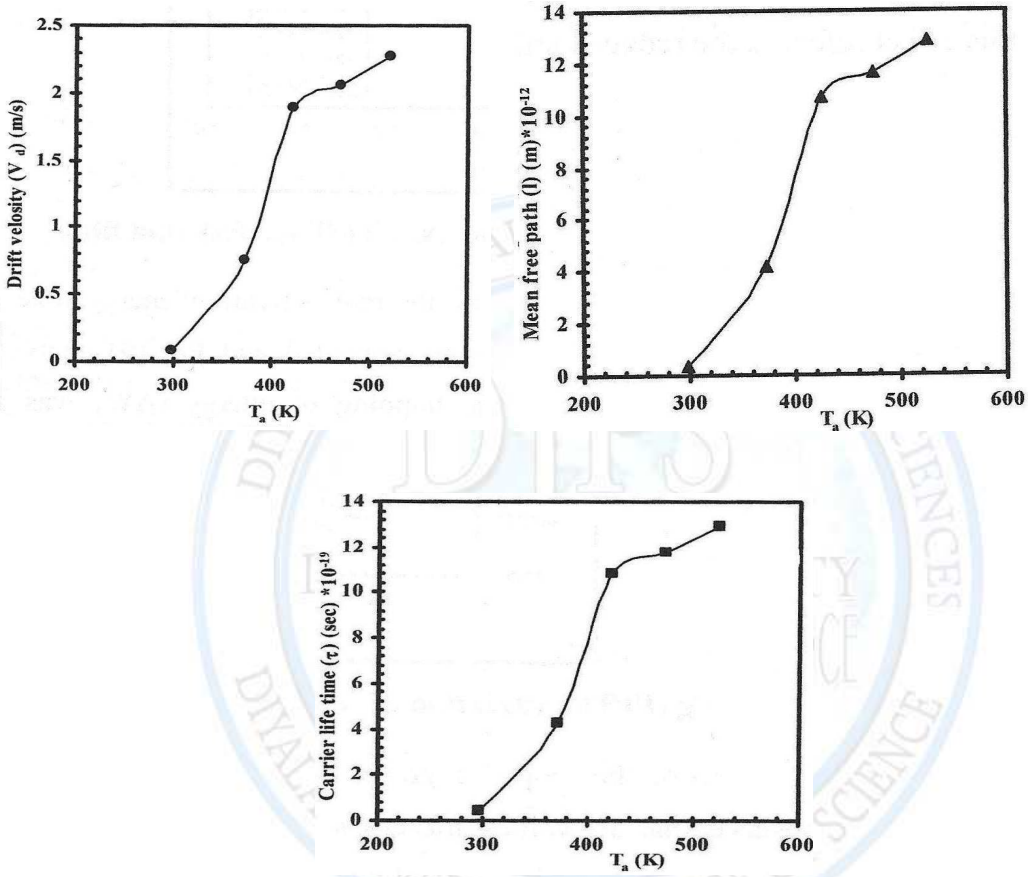


Fig.(7) the variation of a- drift velocity b- carrier life time c- mean free path with annealing temperatures for thin PbS films.

6. Seebeck effect:

The Seebeck coefficient (S) was measured as a function of annealing temperature for polycrystalline PbS films within the range 298- 408 K as shown in figure (8). The Seebeck coefficient is defined by $S=\Delta V/\Delta T$, where ΔV is the Seebeck voltage which depends on the gradient of temperature between the hot and cold terminal of the samples. The thermoelectric power results confirm the results of Hall Effect.

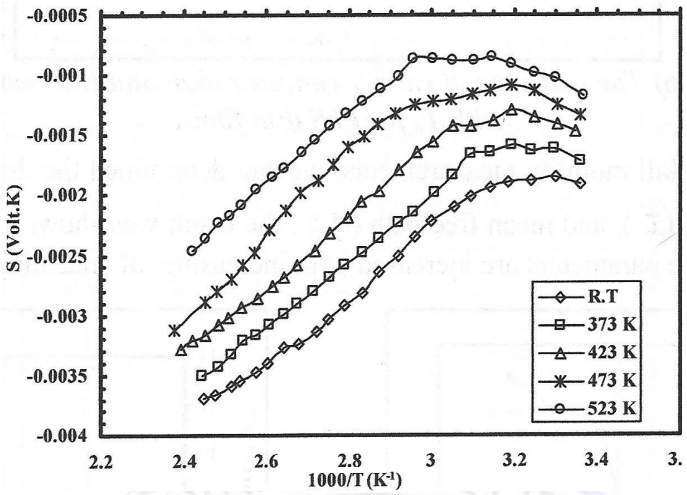


Fig. (8) Seebeck coefficient versus 1000/T at different annealing temperature for PbS thin films

The thermal activation energies (E_S) can be obtained from the slope of curves in figure (8). It can be observed that E_S values increase with increasing the annealing temperature as shown in figure (9). The values of the energies of hopping (ΔW) can be calculated from the difference between E_{a1} and Es and we can (ΔW) observe that increases with increasing T_a as shown in Figure (9), this increasing is due to reduce the tails within the band gap as a result of annealing[8].

Similar results have been observed by many workers such as George[8] and Woods[11], they were showed that polycrystalline PbS films have high Seebeck coefficient compared with the single crystal PbS because of the scattering by potential barriers associated with grain boundaries.

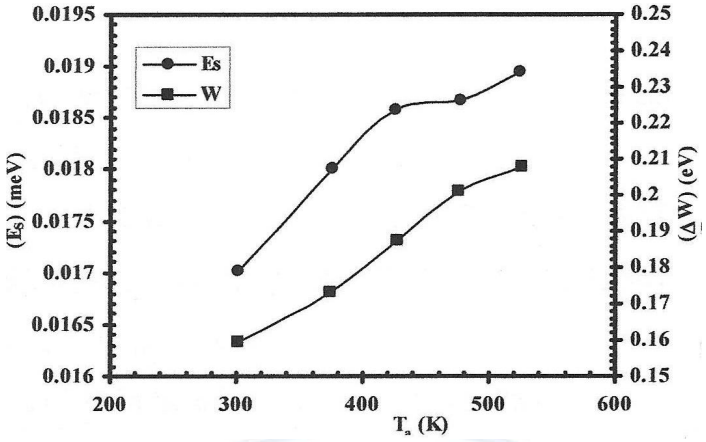


Fig.(9) the variation of E_S and ΔW with annealing temperatures for thin PbS films.

7. Conclusions

A cubic phase polycrystalline PbS alloy have been prepared. The X-ray diffraction spectrum showed dominate orientation at (200) plane. The alloy was evaporating by thermal evaporation technique. The electrical conductivity has been observed to decrease with increasing the annealing temperature, while the activation energies have increased with increasing the annealing temperature of the prepared heat treated thin films. The prepared PbS films were P-type, it can be observed that the carriers concentration decreased with increasing the annealing temperature. While Hall mobility, drift velocity, carrier life time and mean free path were increased with increasing the annealing temperature. In thermoelectric power measurements the sign of the slope remained positive (Fig (8)) which means all films were p-type. The thermal activation energies and the energies of hopping were increased with increasing the annealing temperature.

8. References

1- K. Hideyuki and Sado "journal of applied physics" 83, 11, 1998, 5997- 6000.

2- V. Stancu, M. Buda, L.Pintilie, I. Pintilie, T. Botila and G. Iordache "thin solid films, 516 (2008) 4301- 4306.

3- F.E. Kruis , K. Nielsch, and H. Fissan " J. Appl. Phys. " v 47, no. 4 (1998) p 547.

4- Heini Salmoni "electrodeposition of PbS, PbSe and PbTe thin films" M.Sc. thesis, faculty of science, Uni. Of Helsinki, 2000.

5- J.J. Valenzuela- Jauregui, R.Ramirez-Bon, A. Mendoza-Galvan and M. Sotelo- Larema, "thin solid films " 441 (2003) 104 -110.

6- A. U. Ubale, A.R. Junghare, N.A. Wadibahasmi, A. S. Daryapurkar, R.B. Manker, V.S. Sangawar "Turk Journal of Physics "31 (2007), 279-286.

7- G.H. Mohammad," Fabrication of Pb_xS_{1-x} photoconductive detector and study the effect of annealing temperature on its optoelectronic properties", M.Sc. thesis, collage of science university of Baghdad, 2002.

8- J. George, T.I. Palson and K.S. Joseph, "Solid state communication", 58, 9, 1986, 605.

9- VI. Levechenko and LI. Postnov, "Semiconductors", 30, 12, 1996, 13885.

10- E.M. Al-Fawade," Fabrication of Pb_xS_{1-x} detector", PhD. thesis, collage of science university of Baghdad, 2005.

J.F. Wood, "Phys. Rev.", 106, 2, 1957, 235.