The Effect of Annealing Temperatures on Optical and Electrical Properties of PbTe Thin Films

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Abstract

The study was carried out by the preparing of PbTe thin films and studying the effect of annealing temperatures on electrical and optical properties.
The PbTe thin films have been prepared by thermal evaporation in a vacuum of ($2*10^{-5}$) Torr with thickness 500nm at room temperature and annealed at different annealing temperatures of (373,423,473)K for 30 min.
The electrical measurements show that the PbTe thin films have two kinds of activation energy which increases with increasing annealing temperature.
The Hall Effect measurements prove that thin films are n-type at room temperature and convert to p-type by annealing temperature and it is found that
N_H decreases with increasing annealing temperature but μ_H increases with increasing annealing temperature.
The optical measurements show that the PbTe thin films have direct energy gap which show that energy gap increases with increasing annealing temperatures and it is found the transmittance increases with increasing annealing temperatures

الخلاصة

أجريت الدراسة بتحضير أغشية من تيلريـاد الرصاص ودراسة تـأثير التلدين على خصائصـها والبصرية و الكهربائية.
حضـرت أغشـية تيلريـاد الرصـاص بطريقـة التبخيـر الحـراري تحـت ضـغط(٥- ١٠*٢) تـور. وبسمك(٥٠٠) نانومتر) عند درجة حرارة الغرفة،وعوملت هذه الأغشية بعد ذلك حراريا عند درجات حرارة مختلفة (٣٧٣،٤٢٣،٤٧٣) ولمدة ٣٠ دقيقة.K .
أظهرت القياسات الكهربائية أن أغشية تيليرياد الرصاص تمتلك أثنين من طاقات التنشيط،وتزداد هذه الطاقات مع زيادة درجة حرارة التلدين،أثبت تأثير هول أن الأغشية من النـوع السـالب عند درجة حرارة الغرفة، وتتحول الى النوع الموجب بالتلدين، ووجد أن N_H يقل مع زيادة درجة حرارةالتلدين، تركيزحاملات الشحنة حرارةالتلدين زيادة مع μ_H في حين تزداد التحركية مع زيادة التلدين.
أظهرت القياسات البصرية أن لاغشية تيلرياد الرصـاص فجوة طاقـة مباشـرة مسموحة،ووجد أن فجوة الطاقة تزداد مع زيادة درجة حرارة التلدين،ووجد أن النفاذية تزداد مع زيادة درجه حرارة التلدين.

Introduction

Thin films are extensively used in wafer fabrication, and they can be a resistor, a conductor, an insulator, or even a semiconductor. Thin films behave differently from bulk materials of same chemical composition in several ways. For instance, thin films are sensitive to surface properties while bulk materials generally aren't. (1)
In one way or another most physical properties of films (optical, chemical,

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magnetic, electrical, etc.) are of importance in an ever widening sphere of industrial, scientific and technical application. [2]

Lead chalcogenide, a compound of lead with elements of group VI (sulfur, selenium and tellurium) belongs to a class of semiconducting compounds described by the general formula $A^{IV} B^{VI}$ [3,4].

Lead chalcogenides have many special characteristics in comparison with other semiconductors:

1)The bandgaps are smaller at lower temperatures, i.e. the temperature coefficients of E_g are positive while they are negative in all other elementals or compounds [5]

2)The lattice structure may be very unstoichiometric. The vacancies and interstitials control the conductivity type, an excess of Pb causes n – type conductivity and excess of chalcogenide causes p–type conductivity [5].

3)The band gap of PbS is smaller than the band gap of PbTe, although commonly the band gap in the metal chalcogenide semiconductors diminishes as the chalcogenide increases [5].

4)Large carrier mobilities may be unique among polar compounds and make these semiconductors a very interesting branch of basic physical research [6].

5) Lead chalcogenides are ones of the best thermoelectric materials for working temperature range of 500 – 900 K [7].

Gelmont et al., (1981) have obtained the absorption spectrum near and above the fundamental edge of PbTe films on Baf_2 substrate at 313 K between 2 and 8μm. The thickness of film was (0.61μm) from parallel measurements of transmission and reflection. They found that the direct energy gap at L is 0.321 eV [8].

Saloniemi,(2000)has studied the physical, chemical and electrical properties of PbTe thin films prepared by electrodeposition method . He found: After annealing the films he found the conductivity will be p-type ,and the annealing at 373K does not affect much the resistivities of PbTe which remained between 0.5 – 10 Ω.cm [5].

Khairnar et al., (2002) have prepared PbTe thin films of thickness ranging from (1000– 2500)°A by evaporation technique on to glass substrates at various temperatures.

They found the activation energies of films are evaluated as 0.099, 0.109, 0.102 eV for substrates temperatures (323,373,423) K respectively [9].

This research considers studying PbTe thin film because it is one of the important lead chalcogenide compounds, and has many practical applications in the fields of detectors, semiconductors' laser and diodes.

Therefore the goal of this research is to prepare of PbTe thin films by using thermal evaporation method, and study the effect of annealing temperatures on optical and electrical properties of films

Theoretical Part:

A semiconductor is a material whose conductivity lies between that of conductors and of insulators [3], the conductivity of semiconductor is generally sensitive to temperature, illumination, magnetic field. This sensitivity in conductivity makes the semiconductor one of the most important materials for electronic application [10]. Semiconductorss consist of two bands namly valence and conduction bands which are separated by a forbidden gap[11].This gap is usually quite narrow in semiconductors [12], so that, as the temperature of the semiconductor is increased, some electrons receive energy greater than the gap energy and get transferred to the upper energy band. These electrons now contribute to the conduction [13].

PbTe is used for the fabrication of IR detectors .They have found wide spread application for detection of IR radiation [14]. For pure PbTe the forbidden energy gap decreases as the temperature is lowered [3]..The density of PbTe is (8160) Kg m^{-3} [15].

PbTe has high refractive index of (5.65) in the near infrared [3] and dielectric constant (ε_r=30)[16] . The use of PbTe as the laser material has made it possible to extend spectral range of laser radiation in the direction of wavelength longer than those emitted by InSb laser [4].

Experimental Part:

(A)The Preparation of PbTe Thin Films:

A molybdenum boat is used in evaporation process because it will not react with the evaporated material and it has a melting point greater than that of PbTe (2895K).

The appropriate amount of PbTe powder is selected and measured by using sensitive electrical balance. During the deposition some of the material will be lost by volatilization or expansion from the substrate surface, therefore we should add ~20% in excess of material to be sure that the wanted thickness will be achieved.

The (glass and NaCl) substrates are fixed on the substrate's holder at a distance about 16(cm) above the source of evaporation (boat).

Because of PbTe films work in infrared spectral range, NaCl substrate is used to measure optical properties which can allow the infrared wavelength to transmitted through but glass substrate work to cut the infrared wavelength and allow only invisible wavelength to be transmitted.

When the vacuum in chamber reaches ($2\text{-}3*10^{-5}$) Torr, an electrical current is applied from the power supply passing through the boat.

The rate of deposition is about (0.03125μm/min), which is determined by thickness of sample and period of evaporation. The coating system is left for 24 hours under low pressure to prevent any reaction between the hot boat and air gases, later the samples are extracted and kept in Petri dishes, then placed in a desiccator until measurement. The annealing process was performed in an electrical furnace of the type (precision), and at different temperatures of (373,423,473) K for 30 min period.

(B) The Weight Method:

Weight method is used in measuring prepared PbTe film thickness. This method is one of the classic approximate methods in measuring. The material is weighted using sensitive electrical balance (mentioned in previous paragraph); if the weight of the material is equal to the mass of film and (R) is the distance between the boat and the substrates over which the film will be deposited, the thin film thickness will be according to the relation:[17]

$$t = m / 2\pi R^2\rho \text{ ---------- } (1)$$

Where:

- m : is the mass of the evaporated material (gm)
- ρ : density of alloy (gm/cm^3)

This method is one of the oldest, simplest and least accurate methods, but it has the advantage that it gives average values for film thickness [18].

(C) Optical Measurements:

The FT- IR Spectroscopy type of (8400S Shimapzu) was used to measure the optical properties of PbTe thin films which are deposited on NaCl substrates and annealed at different temperatures of (373, 423,473) K for 30 minutes .The transmittance spectra were measured and found in the range of (2500-5000)nm

(D)Electrical Measurements*:*

The digital electrometer type of (Keithely 616) was used to measure the electrical properties of PbTe thin films which are deposited on glass substrates and annealed at different temperatures of (373, 423,473). The D.C. electrical conductivity was measured in the thermal range of (313-473)K this can be done by putting the films on a electrical furnace of the type (Memmert).

Results and discussion

(1)The effect of annealing temperatures on Transmittance Spectrum:

Fig. (1) shows the effect on annealing temperature in the spectral of transmittance, the percentage of transmittance increases with increasing annealing temperatures .These results agree with B. Li et al. who found that the transmittance of PbTe' filters increases with increasing temperatures and shift at short wavelength [19].

(2)The effect of annealing temperatures on Optical Energy Gap:

The optical energy gap can be determined by using Tauc equation:

$$\alpha h\nu = (Bh\nu - E_g)^r \text{ -----------(2)}$$

αhν: Absorption coefficient at angular frequency (2 π ν)

r = ½, 2/3, 1, 2, 3 depends on electronic transition nature

B: is a constant proportion of density state in valence and conduction bands in amorphous semiconductors.

Figs. (2) a, (2) b, illustrate the variation in $(\alpha h\nu)^{1/2}$ as a function of wavelength.

Our data show E_g^{opt} increases with the increase in annealing temperatures .It is found that E_g^{opt} increases from (0.42)eV for unannealed film to (0.433)eV for film annealed at 473 K.

These results are similar to result of Zemel et al. [20]. They found that the E_g^{opt} increases from 0.31 eV for unannealed films prepared at room temperature to 0.345 eV for film annealed at 373 K. and they agree with those of Mitchell et al. who found the E_g increases from 0.190 ± 0.002 at 4.2 K to o.217 ± 0.002 at 77 K [20]

From table (1) we can observe that E_g^{opt} increases with increasing Ta.

The energy gap broadening in the annealing films may be related to the existence within the band gap of a high density levels with energies near the bands which can give rise to band tailing, as has been suggested for other polycrystalline materials [21].These levels should be associated with the electronic states at grain boundaries and their density should decrease markedly with heat treatment .

The increase in E_g^{opt} may be due to the increase in the grain size which leads to decrease the crystal defects.

(3)The effect of annealing temperatures on Electrical Conductivity:

The change conductivity with temperature indicates that all the film samples have negative temperature coefficient of resistivity which suggests their semiconducting nature.

Fig. (3) shows the conduction dependence on temperature in the range of (313 - 473) K of PbTe films deposited at room temperature and annealed at (373, 423, 473)K for 30 min. As shown from this figure the conductivity displays two mechanisms of charge carriers transport, yielding two activation energies at two thermal ranges.

In the range of (313-393) K the activation energy Ea_1 is produced due to hopping of charge carriers between localized state inside energy gap.

In the range of (403-473)K the activation energy Ea_2 is produced due to transfer charge carriers to a farther distance from extended state beyond mobility edge.

The $\sigma_{R.T}$ is found to decrease with increasing annealing temperatures. It is found that the conductivity of PbTe films deposited at room temperature decreased from (0.125) $(\Omega.cm)^{-1}$ for unannealed films to (0.0175) $(\Omega.cm)^{-1}$ for films annealed at 473 K, see table (2).These results regardless of numerical values agree with that of Putly who found that the conductivity of PbTe decreases from 94.4 $(\Omega.cm)^{-1}$ at 20 K to 5.5 $(\Omega.cm)^{-1}$ at 290 K [22]. These results also agree with the results of Saloniemi[5]. He has prepared the PbTe films by electrodeposition at room temperature. He found that conductivity decreases from 5$(\Omega.cm)^{-1}$ for unannealed films to 1$(\Omega.cm)^{-1}$ for films annealed for five hours.

The decrease in $\sigma_{R.T}$ with increasing annealing temperatures is attributed to the decrease in the crystalline defects which leads to increase the energy gap and decrease the concentration of carriers [21, 23].

(4)*The effect of annealing temperatures on Hall Effect*

The purpose of Hall Effect measurement is to obtain the carriers' type and concentration of PbTe thin films deposited at room temperature and annealed at different temperatures.

Hall effect is negative for PbTe thin films deposited at room temperature, which means that the films have n–type conduction, after annealing the films change to p–type conduction, this is due to that annealing leads to an excess Pb atom which produces one free electron in the conduction band and an excess Te atom which produces one free hole in the valence band, this drives a PbTe thin film from n–type conduction to p–type conduction [24].

Our results agree with the results of Abd El-Ati [25]. He prepared PbTe thin films by evaporation under vacuum pressure of 10^{-5} Torr. The charge carriers were (n–type) and converted to (p–type) by exposing them to heat treatment.

Fig. (6) shows the effect of temperature on Hall coefficient R_H for PbTe thin films deposited at room temperature and annealed at different temperatures. We can see that Hall coefficient increases with increase in Ta (373,423, 473) K for all samples.

Fig. (7) shows the variation in carrier concentration (N_H) of PbTe films with Ta. It is found that N_H decreases with increasing annealing temperatures it decreases from ($2.84*10^{17}$) for unannealed films at room temperature to ($0.069*10^{17}$) for films annealed at 473 K. These result agree with that of Putley who found that carrier concentration decreases from ($2.08 * 10^{19}$) at 77K t ($0.12 * 10^{19}$) at 290 K [22].

Conclusions

(1) Optical Properties

A) The result of optical energy gap shows that PbTe thin films have only allowed direct transition with r equal to ½, the optical energy gap of PbTe thin films is affected by annealing process and increases with increase in annealing temperatures , it increases from (0.42)at R.T to (0.433)at 473K.

B) The results of optical measurements show that the transmission increases with increasing annealing temperatures, it increases from (31.11%) at R.T to (46.81%) at 473K

(2) Electrical Measurements:

A) The electrical conductivity decreases with increasing annealing temperatures, it decreases from (0.125) at R.T to (0.0175) at 473 K.

B) The results show that PbTe thin films have two activation energies, Ea_1 decreases with increasing annealing temperatures, it decreases from (3.01) at R.T to (4.34) at 473 K but Ea_2 increases with increasing annealing temperatures it increases from (0.247) at R.T to (0.277) at 473 K

C) Hall Measurements show that PbTe thin films are n-type and change to p-type after annealing from 373 to 473 K.

R_H increases with increasing annealing, it increases from (22) at R.T to (89) at 473K, N_H decreases with increasing annealing temperature, it decreases from ($2.84*10^{17}$) at R.T to ($0.096*10^{17}$) at 473K but μ_H decreases with increasing annealing temperature. it decreases from (2.574)at R.T to (1.557) at 473K.

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Table (1) The optical properties of PbTe thin films deposited at room temperature and annealed at different temperatures.

Ta (K)	E_g (eV)	T % at $\lambda = 3500$ nm
R.T.	0.42	31.11
373K	0.428	38.5
423K	0.432	44.69
473K	0.433	46.81

Table (2) The electrical properties of PbTe thin films deposited at room temperature and annealed at different temperatures.

Ta (K)	$\sigma_{R.T}$ $(\Omega.cm)^{-1}$	Ea_1	Ea_2	R_H $(cm^3.col^{-1})$	N_H*10^{17} (cm^{-3})
R.T	0.125	3.01	0.247	22	2.84
373	0.059	3.45	0.255	35	1.78
423	0.037	3.69	0.259	51	0.122
473	0.0175	4.34	0.277	89	0.096

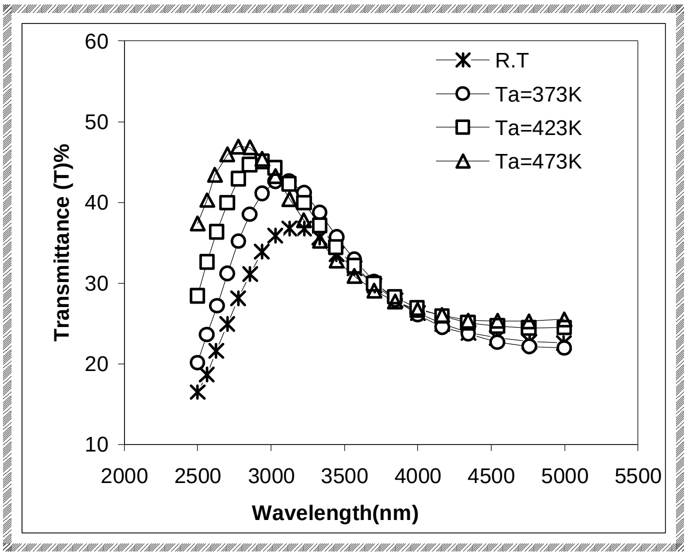

Figure (1) shows the transmittance as a function of wavelength of PbTe thin films deposited at room temperatures and annealed at different temperatures

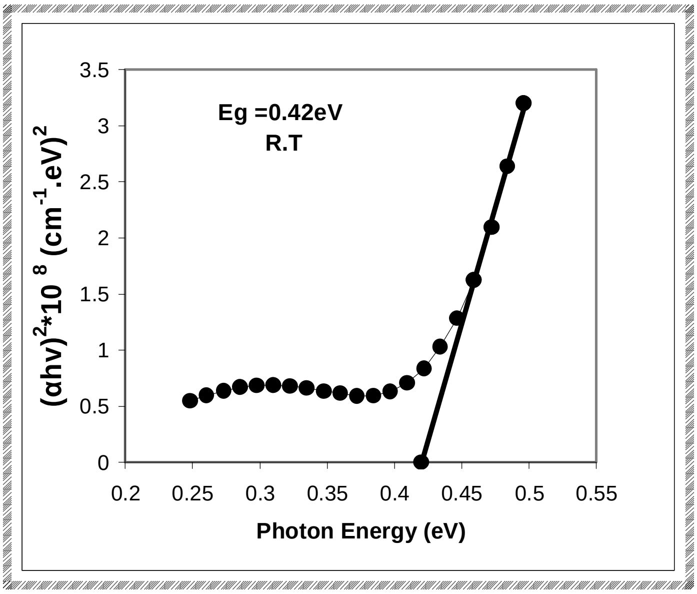

Figure (2) a

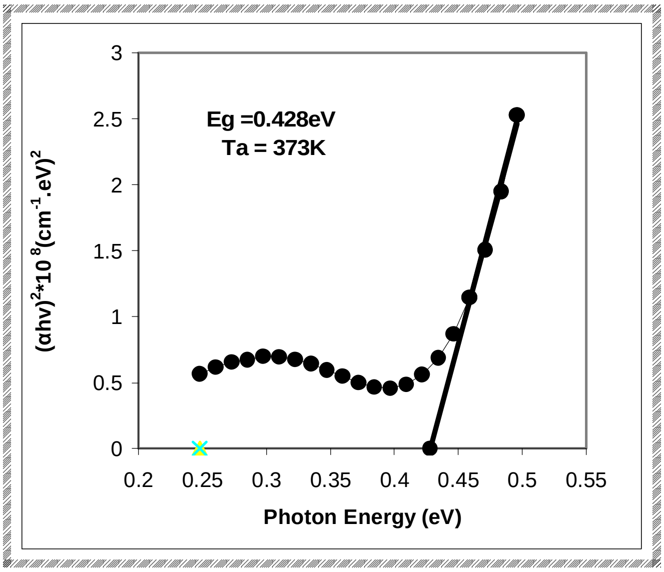

Figure 2 (b)

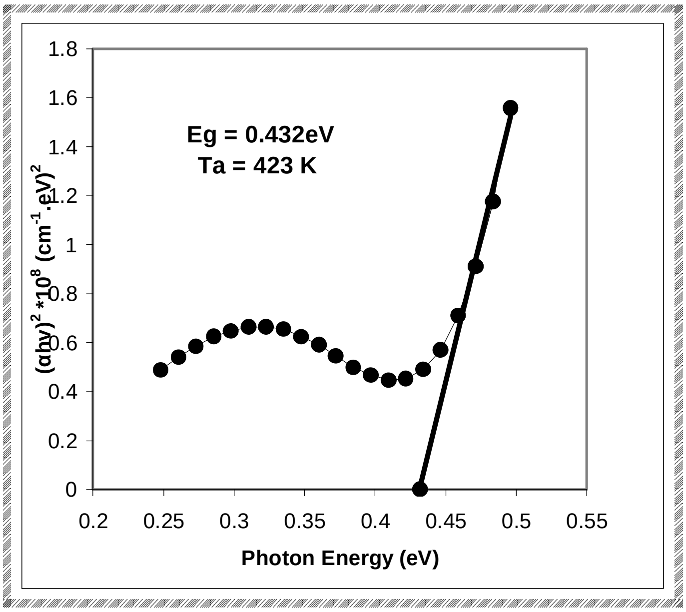

Figure (2) d

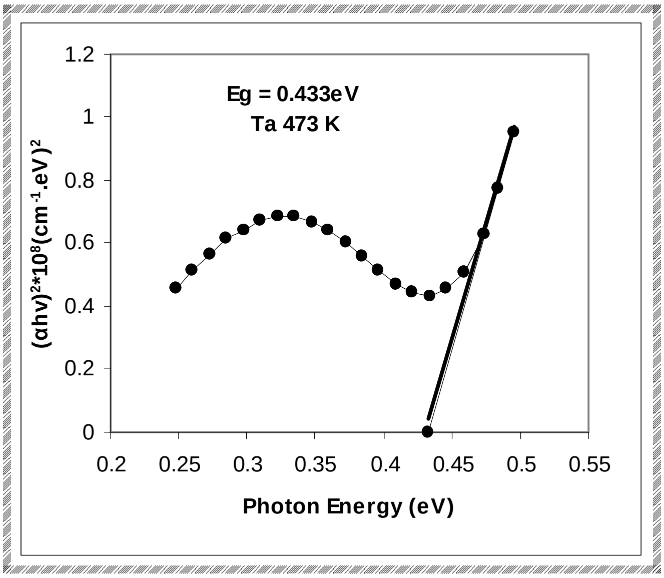

Figure (2) c

These figures show the variation in $(\alpha h\nu)^2$ with (hν) for PbTe thin films deposited at room temperature and annealed at different temperatures.

At a. Ta =R.T b. Ta = 373K c. Ta = 423K d. Ta = 473 K

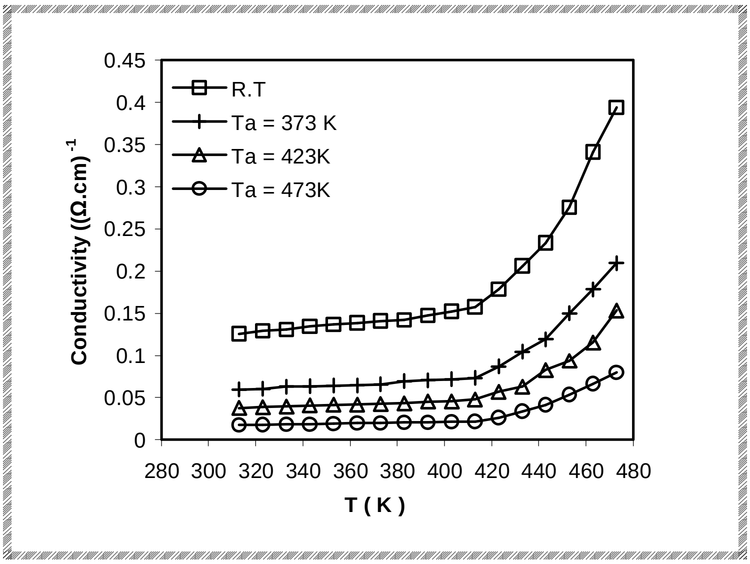

Figure (3) Variation in conductivity with temperature of PbTe thin films deposited at room temperature and annealed at different temperatures

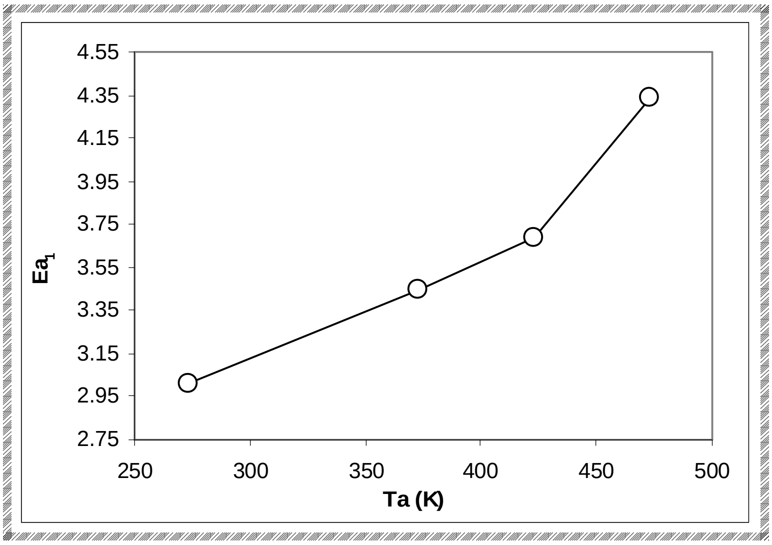

Figure (4) The variation in Ea_1 with Ta for PbTe films

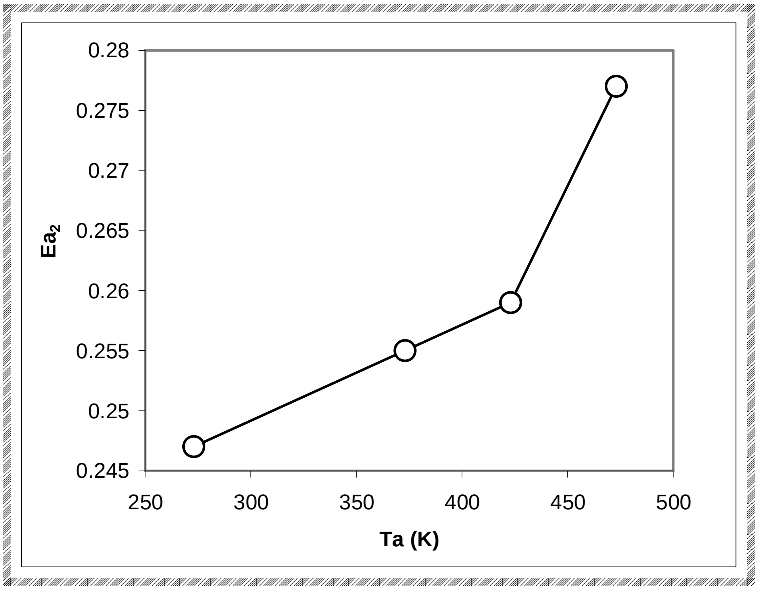

Figure (5) The variation in Ea_2 with Ta for PbTe films

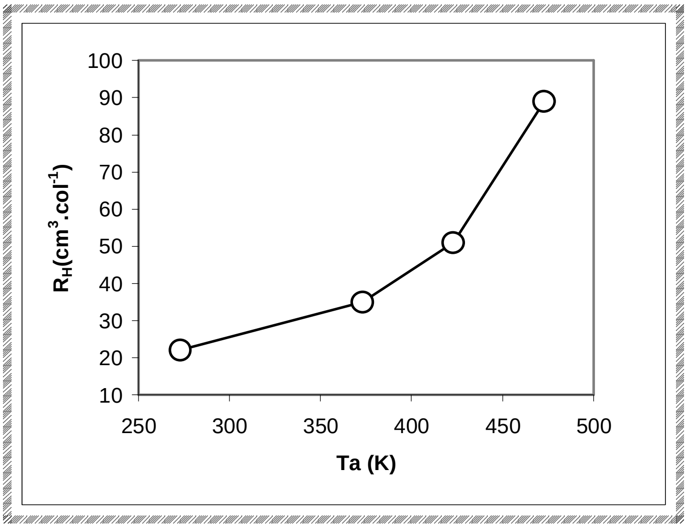

Figure (6) The variation in R_H with Ta of PbTe thin films deposited at room temperature and annealed at different temperatures.

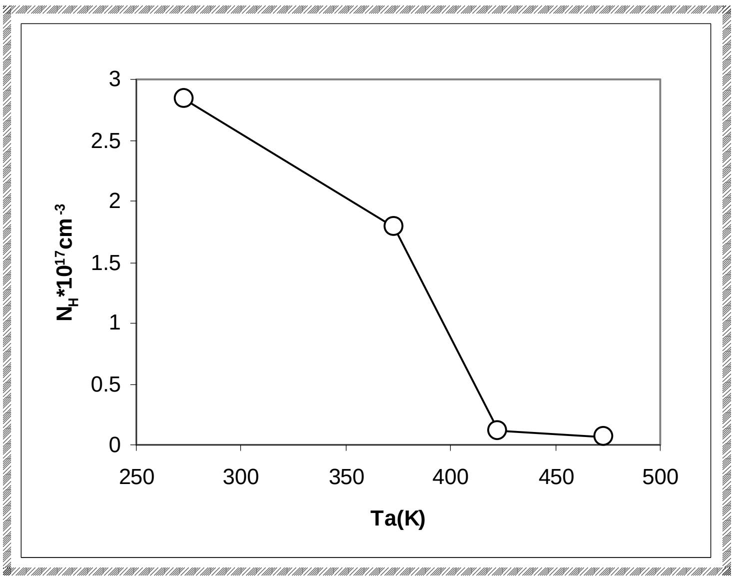

Figure (7) The variation in N_H with Ta of PbTe thin films deposited at room temperature and annealed at different temperatures.