أثر المعالجة الحرارية على الخصائص التركيبية والكهربائية لأغشية ZnS الرقيقة

ا.م سوسن عبد الزهرة

كلية التربية الأساسية/قسم العلوم/الجامعة المستنصرية

تقديم البحث :- 20 /2011/6

قبول النشر:- 2011/11/2

الخلاصة:

تناولت الدراسة تأثير التلدين على الخصائص التركيبية والكهربائية لأغشية ZnS الرقيقة المحضرة بطريقة التحلل الكيميائي الحراري،وتم تحليل النتائج باستخدام حيود الأشعة السينية ودراسة تأثير هول، أظهرت نتائج فحوصات الأشعة السينية بأن الأغشية المحضرة هي من النوع متعدد التبلور وذات طور سداسي ، وان هناك زيادة في درجة التبلور بعد المعالجة الحرارية حيث ازداد حجم الحبيبات البلورية وكانت عند القيم nm(18-40)وانخفضت قيم كثافة الانحراف(δ(dislocation density

ضمن الحدود lines/cm (1.6×10^{12}- 1.01×10^{12}) ، ولوحظ تغير المقاومية

الكهربائية مع الحرارة، إذ انخفضت المقاومية بمقدار ثلاث مرات عن قيمتها قبل التلدين ، بالإضافة إلى تغير قيمة طاقة التنشيط بقيم تتراوح بين eV(1.5- 1.11) مع المعالجة الحرارية. ومن نتائج هول اتضح بأن الأغشية المحضرة هي من النوع السالب وذات تحركيه بحدود $160\pm10 cm^2/v.s$. وهذه النتائج تؤكد حدوث تحسن في التركيب البلوري للأغشية بعد المعالجة الحرارية عند درجات °C(400,500) نتيجة لتقليل العيوب البلورية.

Influence of Heat Treatment on the Structural and Electrical Properties of ZnS Thin Films

Sawsan Abdul Zahra

College of Basic Education ,Science Department

Al-Mustasirya University

Abstract:

Zinc Sulfide thin films have been deposited onto glass substrates by spray pyrolysis method, the films were analyzed by X-ray diffraction and Hall Effect measurments.XRD analysis of the deposited and annealed films showed that all the films have polycrystalline with hexagonal structure. The effect of heat treatment enhances the grain size and improves the crystalline of the films, the grain size is found to increased from (18-40)nm, also the dislocation density (δ)decreased and in the range (1.6×10^{12} -1.01×10^{12})lines/cm. Electrical resistivity is changed after the films were exposed to heat treatment, the value of resistivity was decreased about (3) times than that before annealing. Moreover the activation energy was decreased (1.5-1.1)eV by heat treatment .Hall measurements proved that ZnS thin film is an n-type semiconductor with electron mobility around 160±10cm^2/v.s. These results confirmed the improvement in crystallinity of the films with heat treatment at (400,500) °C because of decreasing crystal defects.

Key wards: ZnS thin films, structure, electrical properties, spray pyrolysis.

Introduction:

The II-VI group semiconductors are of great importance and this due to their applications in various applications among these, Zinc Sulfide thin film, is the most suitable for its utility in opto-electronic devices .ZnS has many advantages such as, high deposition rate, transparency at R.T

due to the broad band gap (~3.7eV) and less sensitive about oxidation than ZnO[1],there has been a great interest in the study of charge carrier transport of ZnS which has become one of the most applied insulator in thin film electroluminescence devices[2].ZnS is suitable for use in blue light emitting diodes ,it has high refractive index about (2.35) [3]. polycrystalline and nanocrystalline ZnS have received much attention lately because of its probable important role in photovoltaic technology ,optical coating ,n-window layers for thin film hetrojunction solar cell[4] ZnS has a low exaction Bohr radius (2.5nm) that makes it nanoparticles interesting as small biomolecular probes for florescence and laser scanning microscopy [5].several techniques have been used to produce ZnS thin films such ,sputtering[6],chemical Bath [7]vacuum evaporating technique [8]spray pyrolysis method[9].In this work ,we report how thin films of ZnS were deposited on glass substrate using spray pyrolysis method ,this method has been classified as one of the best cost effective techniques of thin films deposition .It is simple ,cheap and easily reproducible and through it large area of thin films can be deposited without using sophisticated equipment. Structural and electrical properties have been studied of ZnS thin film as function of annealing temperature.

Experimental:

ZnS thin films were prepared by spray pyrolysis method using aqueous solution of zinc chloride and thoiurea at molar ratio of 1:1, continuous film is formed on the hot substrate (350°C) by thermal decomposition of the material, the films deposited below 350°C are amorphous. Thickness of the film was measured by weight method and was 3000Å. Spray rate employed was 3ml/min, the obtained films were white to yellow, uniform and with good adherence to the substrate. The films were characterized by XRD and Hall Effect measurements, included the effect of heat treatment on the structure of the examined films. Thermal annealing of the films were done at different temperatures (400,450,500,550)°C for 3hours by using an oven kind (L_7C-Manfredi) in air atmosphere ,then the films were allowed to cool .Electrical properties

of the films were carried out by monitoring the variation of electrical resistance(R) as function of temperature in the range (27to 177)°C. Mobility and carrier concentration were determined by four –point probe in van der pauw configuration using uniform magnetic field of about 0.215T.The experimental errors were estimated to be in the order of 2.5% compared with the previous letters [10, 11].

Results and Discussion:

Structural Properties: XRD patterns of the as-deposited and annealed ZnS thin films are shown in Fig. (1), it can be seen that the films have polycrystalline hexagonal structure with strong (008) plane, and three subsidiary peaks of relatively low density corresponding to the (104),(105) and (106) planes are also observed, it can be estimated that the position of diffraction peaks is shifted toward higher 2Θ compared with that of the as- deposited film, this peak shifting may be attributed to the residual stress stemming from different expansion coefficient of the film and the substrate [12]. During heating process, several mechanisms undergo in the films 1) recrystallization of ZnS films, 2) replacement of S with O by thermal diffusion, and 3) densification. It can be seen from Fig.(1) that at annealing temperature (400,500)°C, the grain growth results in smoothing the surface and consequently a reduction in surface defect states, hence high intense peak ,but at t=(450 ,550)°C there is a decrease in the peaks intensity, broadening of the peaks and decrease in the grain size this result can be attributed to the film nature (porosity, texture) also XRD measurements indicate that ZnS film may be transform to mixed ZnS and ZnO at these temperatures(the heat treatment did not terminate the Zn-S bonds completely) these results were inconsistent with previous works[13,14] .The C-axis lattice parameters were obtained from the d-interplanner spacing of different peaks and XRD patterns using the equation[15]:

$$d_{hkl}=a/ (h^2+k^2+ (a/c)^2 l^2)^{1/2} \text{ ---------------------(1)}$$

Where (hkl) are the reflection planes ,the value of (c) for all the peaks was 24.92Å after annealing process and the values of(a) decreased

slightly from (3.880to3.707)Å, a decrease in lattice constant of the film is expected due to the increase in the diffraction angle. The dislocation density (δ) was determined using the relation [16] :

$$\delta=15\beta /4aD \quad (2)$$

Where β is the full width at half maximum and D is the grain size which was measured by using Dbye Scherer's formula [17]:

$$D=0.94\lambda/\beta\cos\theta \quad (3)$$

Where λ=1.54Å is the wavelength of x-ray. The calculated parameter (a), grain size (D) and dislocation density (δ) after heat treatment are listed in table (1)

Table (1) :XRD data for the as- deposited and annealed films:

As-deposited zns thin film				Annealed film at 400°C				hkl
2Θ°	a(Å)	D(nm)	δ*10^12line/cm	2Θ	a(A)	D(nm)	δ *10^12line/cm	
29.4356	3.802	18	1.9.	29.4936	3.807	31	1.36	104
47.7869	3.813	25	1.8	48.7879	3.869	39	1.15	008
57.7654	3.815	23	1.8	57.8766	3.811	36	1.35	106
Annealed film at 450°C				Annealed film at 500°C				hkl
2Θ	a(Å)	D(nm)	δ*10^12line/cm	2Θ	a(Å)	D(nm)	δ*10^12lne/cm	
29.9798	3.725	22	1.56	29.9996	3.811	35	1.25	104
48.9987	3.709	35	1.21	49	3.880	40	1.01	008
57.9879	3.707	25	1.31	58.1999	3.816	38	1.11	106

It was observed that the dislocation density are lowered, the grain size are increased with the heat treatment at t=(400,500)°C, this may be due to improvement in crystyallinity and the quality of the films. **Electrical Properties**: The resistivity was determined from the relation:

$$R=\rho l/A \quad (4)$$

where l is the distance between two electrodes ,and A is the product of length of the electrode and thickness of the film. The temperature dependence of the resistivity ρ is given by :

$$\rho=\rho_\circ e^{Ea/KT} \quad (5)$$

where $\rho_\circ$ is the pre-exponential factor ,E_a is the activation energy of the electrical conduction .Fig (2) shows the relation of log ρ against 1000/T for the as-deposited and annealed films at (400,450,500,550) °C in the air

atmosphere ,it can be seen that the as-deposited and heated films have the same behavior of resistivity, that decreases with increasing temperature ,but the resistivity of the as-deposited is larger than that of the annealed films ,the rate of decrease in ρ in the high temperature region is greater than that in the low temperature region, this result shows that the films are semiconducting in nature. The resistivity of the films decreased about three times than the as- deposited film after heat treatment as shown in Fig.(3) where ρ decreased from (40.4to4.5)kΩ.cm. The activation energy is determined from the corresponding slopes of logρ against 1000/T. Fig(4)shows the dependence of E_a on the annealing temperature, activation energy values are of the order (1.5 -1.11)eV, the structural and activation energy studies support the decrease in ρ due to the improvement in crystallinity of the film which is attributed to the filling of discrete of traps lying at or below the Fermi level, which would increase the charge carrier mobility and decrease in defect levels[18] . The carrier concentration(N) can be determined from Hall effect measurements as found in the previous our letter[19] by using the relation $N=1/eR_H$ where R_H is the Hall coefficient and e is the electronic charge. The result indicates n-type conduction. From Fig. (5) and Fig. (6) it can be observed that the films exhibited electron mobility in the range of $160\pm10 cm^2/vs$. and carrier concentration around $(10\pm3)\times10^{15}/cm^3$, the effect of heat treatment is an enhancement in the free carriers and hall mobility, which is probably due to the donor –acceptor band transition where excess Zn acts as donor and some impurity or defects present at surface and interface of the film acts as acceptor [20]. Fig (7) shows the dependence of the activation energy on the carrier concentration so the decrease in the activation energy leads to increase in the carrier concentration. Similar behaviors were reported by several workers [21]. It can be estimated that the heat treatment has an important influence in the structure and electrical properties of the films.

Conclusions:

ZnS films show hexagonal structure, we studied the influence of annealing on the structure and the electrical properties of ZnS thin films. Results show that heat treatment changed the grain size and decreased

the dislocation density which means decreasing in crystal defects, also the resistivity and the activation energy were decreased, moreover hall mobility and carrier concentration were increased with the heat treatment. It is observed that the heat treatment has an important influence in the structure and electrical properties of the films.

References:

1-M.A.Redwanal.I.Soliman.(Study of Electrical and Optical Properties of $Cd_{1-x}Zn_{x}S$ Thin Films), J.of Materials Sci, Vol.38,(2003) P.3449.

2-K.r.Murali .J.Abirami.T.balasubramanian ,(Pulse Plated ZnS Films and their Characteristics), J Mater Sci:Mater Electron, 9225-5, (2008),P.217.

3-M.Y,Nadeem,Waqas AHmed.(Optical Properties of ZnS Thin Films) Turky.J.Phys Vol.24,(2000),P651.

4-J.P.Boraah,K.C.Sarma, (Optical and Opto-electronic Properties of ZnS Nanostructured Thin Film), Acta Ohysica Polonica ANo.4, Vol.114((2008)p.713.

5-Y.C.Zhu,Y.Bondo,Appl.Physc.Lett.82,(2003),P.1769.

6-D.Ghoneim, (Influence of Zn on Optical ,Electrical and Structural Properties of ($Zn_{x}Cd_{1-x}S$ Films) Chacogenide Letters Vol.7,No.6,(2010),P.413.

7-S.HMohamed.M.Hagaryand Emam-Ismail.J.of phys.D.Appl.Phys,4307, (2010),5401.

8-Pawa Kumer,Arravined Kumal,Indian, J.oF Pure and Appl.Phys.vol.44, (2006)P690.

9-A.Abrutis,G.Valincins,G.Baltranas,Thin Solid Films,Vol.515,(2007) ,P6817.

10- A.Uuble and Dk.Kulkarni Bull.(Preparation and Study of Thickness Dependent Electrical Characteristictics of ZnS Thin films) Mater.Sci, Vol.28,No.1, (2005),P.43.

11-F.C.Gumus,M.Zor,J.Cryst.Growth,299,(2007),P.136.
12-A.Ashour,H.H.Afifi,S.A,Thin Solid Films,248, (1994),P.253.

13-Liq Ghalb Subhy. Theses,(Study the Effect of Annealing process on the structure and optical properties of ZnS thin films prepared by the chemical spray pyrolysis) , (2009),phys.dep. Eduacation collage,Al-Mustansirya Unv.

14-Abrutis,G.Valincins.ThinSoldFilms,Vol.515,(2007),P.6817.
15- B.D.CullityandS.R.Stock, Elements of X-ray diffraction,, third edition, prentice Hall., New Jersey, (2001),P4.

16- M.Miyake,K.Murase,T.Hirato.J.Electroanal.Chem,247, (2004),P562
17- Sirotin and M.Shaskolskaya, (Fundamental Of Crystal Physcis) ,(1982)Mir Publishers ,Moscow.

18-F. Gode, C. Gumus, M. ZorJ. Cryst. Growth,299,(2007) , P136 .

19- N. A.Hassan,S.A.Al,Zahra., (Improved Electrical Conductivity of ZnO:Al Films by Using dc Sputtering Technique), J,of the college of basic education ,vol.17,no.69,(2011, p246.

20-M.Rezaee Rokn-Abdadi., (Numerical calculation of the electron mobility in ZnS and ZnSe semiconductors using the iterative method) International J,of the Physical Sci., Vol.5(11) ,(2011),P.1752.

21-A.H.Eid,S.M Salm,J.Of Appl.Sci. Research, 6(6), (2010),P777.

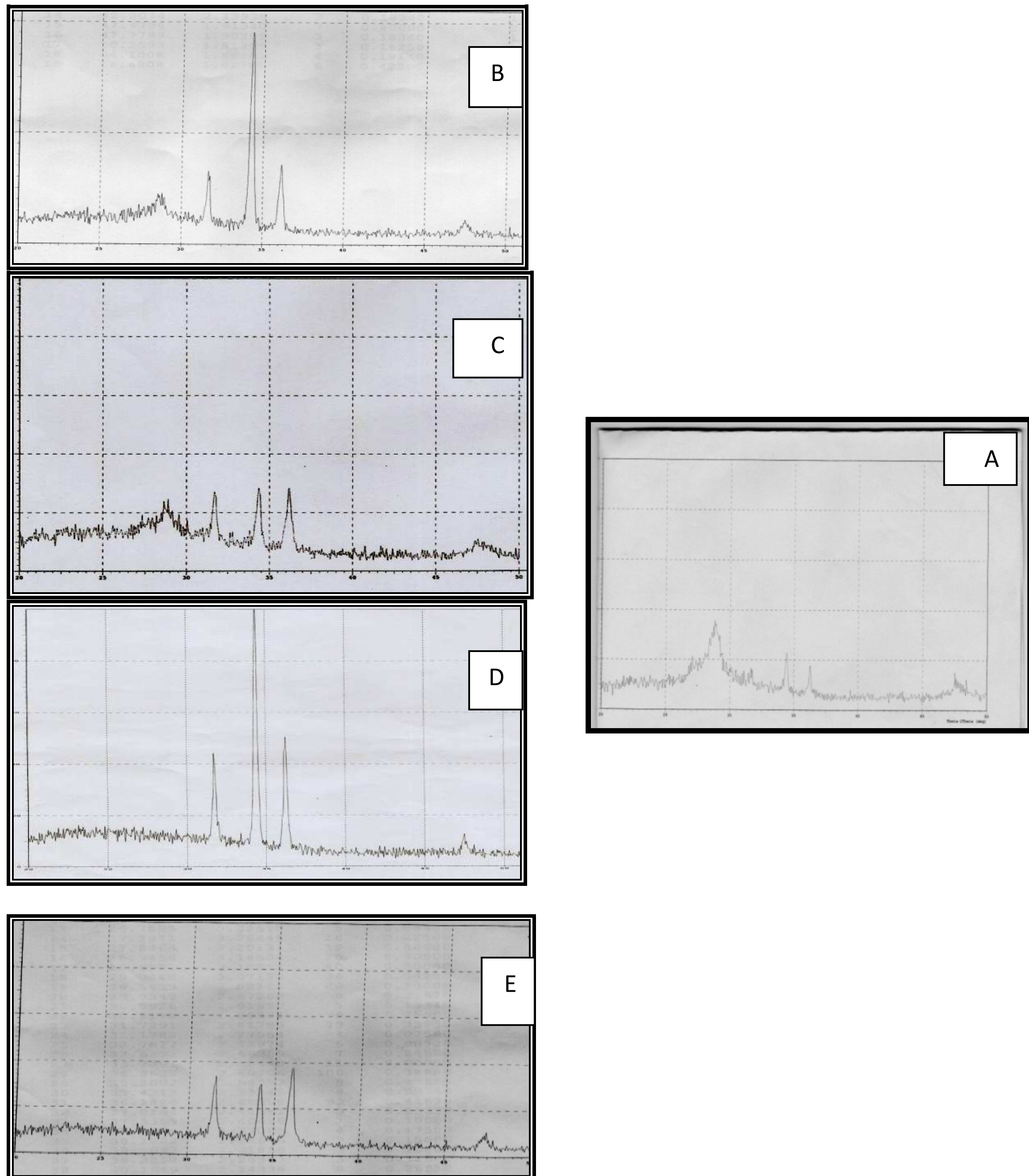

Fig. (1) XRD pattern for ZnS thin film at (A) as-deposited ,(B)t=400°C (C)t=450°C (D)t=500°C(E)t=550°C

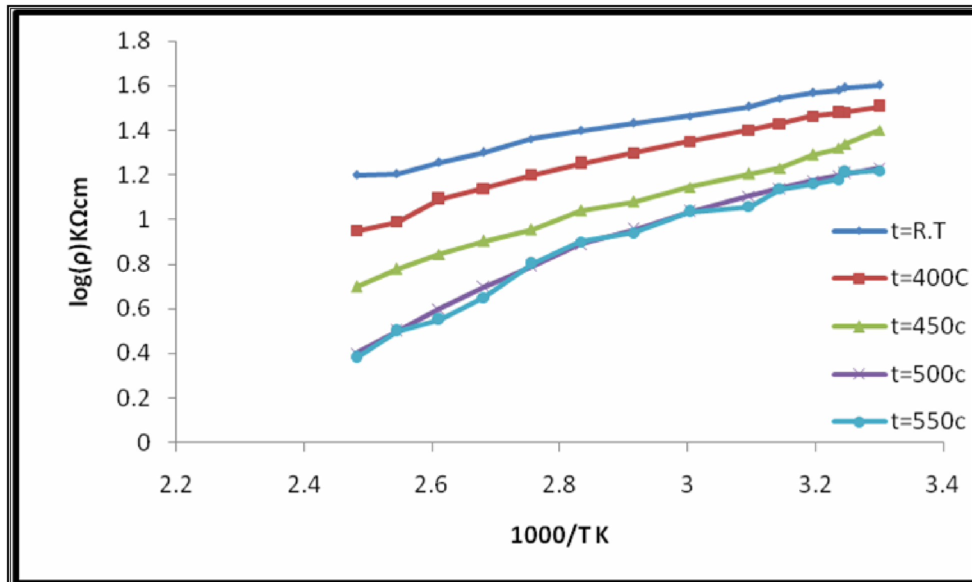

Fig. (2) the dependance of the log(resistivity) against 1/T (k^{-1})of the ZnS thin films

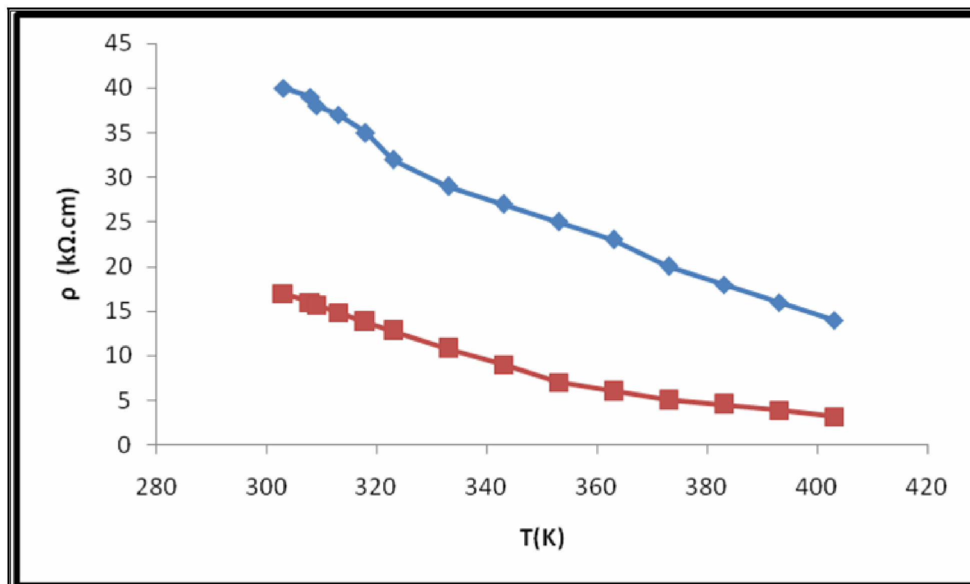

Fig. (3) the behavior of the resistivity with the temperature (A) for the as-deposited film (B) for the annealed film at 500 °C

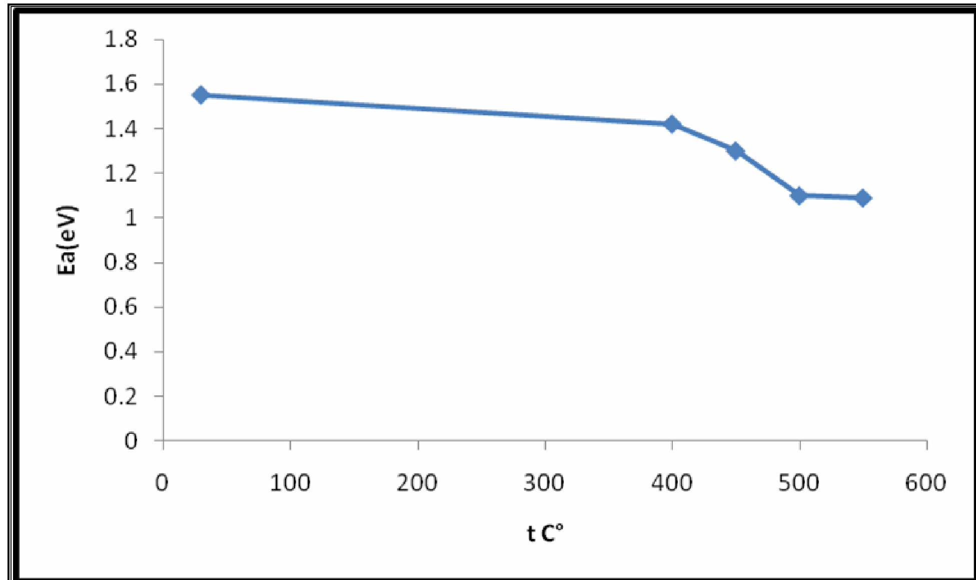

Fig. (4) the dependence of the activation energy on the annealing temperature

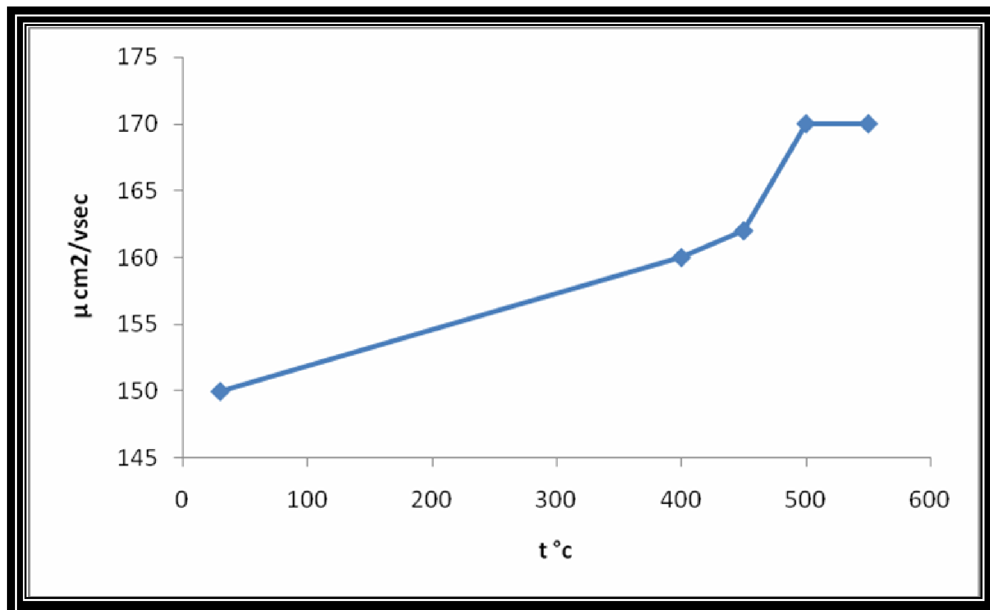

Fig. (5)The behavior of the Hall mobility with the annealing temperature

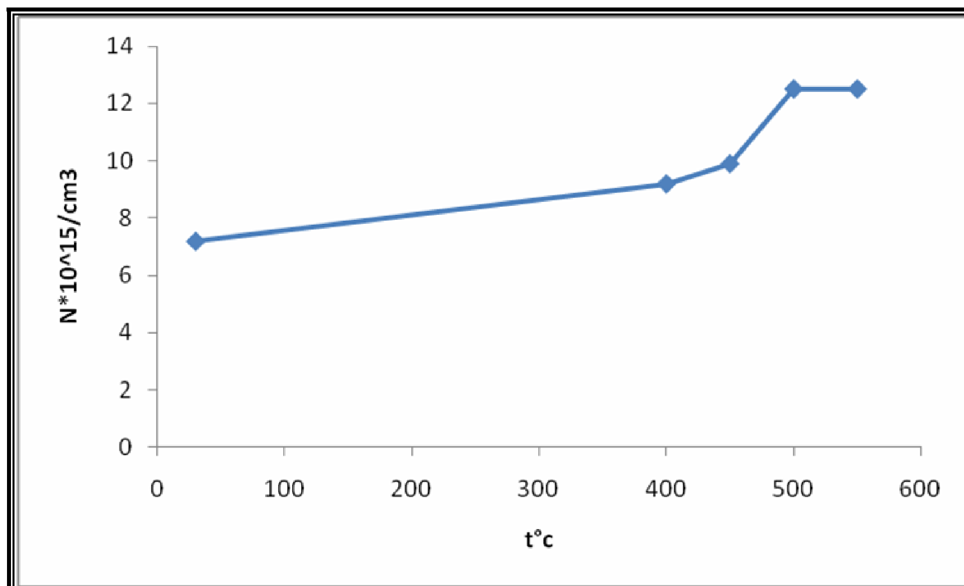

Fig. (6) the behavior of the carrier concentration with the annealing temp.

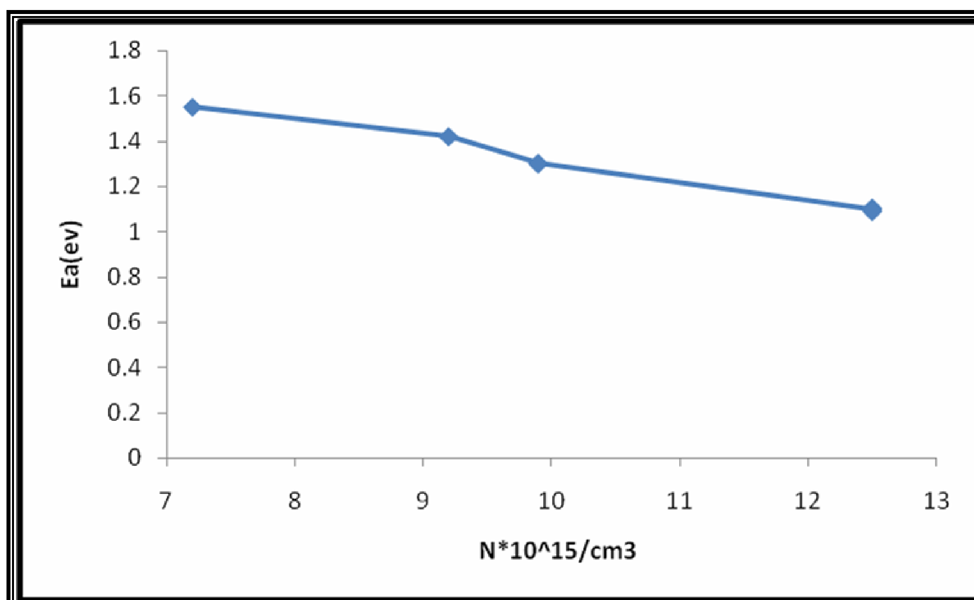

Fig. (7) the dependence of the activation energy on the carrier concentration