Preparation and Study the Electrical Properties of $Sb_{2(1-x)}Se_{3x}$ Thin Films by Pulse Laser Deposition Technique

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Abstract

The alloys of $Sb_{2(1-x)}Se_{3x}$ were prepared by quenching technique with different concentrations of Se (x = 0.1, 0.3 and 0.5). Thin films of these alloys were prepared using pulsed laser deposition (PLD) technique under vacuum of 10^{-3} mbar on glass substrates at room temperature and different annealing temperatures (373 and 473) K with Nd:YAG pulse laser of wavelength (1064 nm), which enabled quality factor of a repetitive rate (6 Hz) and pulse duration (10 ns) and energy laser (1000 mJ).. The D.C measurements declared two activation energy and hence two transport mechanism for $Sb_{2(1-x)}Se_{3x}$ thin films. The values of activation energies increase while σ_{RT} decreases with increasing of concentration of Se and the activation energies decrease while σ_{RT} increases with increasing of annealing temperatures. Hall effect measurements show that the $Sb_{2(1-x)}Se_{3x}$ thin films p-type. Concentration of charge carriers n_H increases with increasing concentration of Se, also charge carriers n_H decreases with increasing of annealing temperatures, while the mobility μ_H and the conductivity (σ) showed opposite behavior to that.

Keywords: Pulse Laser Deposition, Hall Effect , Electrical Conductivity , Activation Energy.

الخلاصـــة

تم تحضير عينات من سبائك $Sb_{2(1-x)}Se_{3x}$ بطريقة التبريد السريع ولنسب مختلفة من تركيز Se (x =0.1 و 0.3 و 0.5). وحضرت اغشية رقيقة باستخدام تقنية الترسيب بالليزر النبضي على أرضيات من الزجاج عند ضغط 10^{-3} ملي بار عند درجة حرارة الغرفة وتم تلدين الاغشية بدرجات حرارة 373 و 473 كلفن بأستخدام ليزر نديميوم – ياك ذو عامل نوعية بمعدل تكرار (6Hz) وزمن تكرار (10s) وطاقة ليزر (1000mJ) . قياسات التوصيلية المستمرة أظهرت أن هنالك اليتي انتقال وبالتالي طاقتا تنشيط Ea_1 , Ea_2. كانت قيم طاقات التنشيط تزداد بينما التوصيلية الكهربائية تتناقص مع زيادة تركيز Se , قيم طاقات التنشيط تتناقص بينما التوصيلية الكهربائية تزداد مع زيادة درجة الحرارة. بينت قياسات تاثيرهول أن اغشية $Sb_{2(1-x)}Se_{3x}$ كانت من نوع p تركيز الحاملات الشحنة تزداد مع زيادة تركيز Se وتتناقص مع زيادة درجات حرارة التلدين , بينما أظهرت التحركية و التوصيلية الكهربائية سلوكاً معاكسا لذلك.

الكلمات المفتاحية: الترسيب بالليزر التبضي، تأثير هول، التوصيلية الكهربائية، طاقة التنشيط.

1. Introduction

Antimony selenide Sb_2Se_3 belongs to V–VI family with orthorhombic crystal structure, in which each Sb- atom and each Se-atom is bound to three atoms of the opposite kind that are then held together in the crystal by weak secondary bonds [Madelung , (2004)]. And it is semiconductor as a promising material with potential applications in thermoelectric devices [Kim and Hyun, (2000)], solar cells [Rajpure, *et.al*., (1997)], photoelectrochemical cells [Sankapal and Lokhande, (2001)], optical recording material [Jayakumar *et.al*., (1995)], lithium ion battery materials [Zhe, and Fu, (2008)] and hydrogen storage materials [Ma, *et.al*., (2009)] due to its good optical and electrical properties. Several methods have been employed to obtain Sb_2Se_3 thin films, such as vacuum thermal evaporation [El-Sayad, (2008)], chemical bath deposition [Rodrı *et. al*., (2005)], successive ionic layer adsorption and reaction methods [Lokhande, *et. al*., (2001)], spray pyrolysis [Rajpure, and Bhosale , (2000)], reactive pulsed laser deposition [Zhe, and Fu, (2008)] and electrodeposition [Torane, *et.al*., (1999)]. Of these methods, PLD (pulsed laser deposition) method is considered as a very effective method to grow high-quality films with complex composition. Additionally, thin films deposited by PLD can result in better crystal structure at lower temperature than by other techniques, which is caused by the higher energy of the ablated particles in the laser-produced plasma plume [Hu Ws, *et.al.*, (1997)].

2. Experimental work

2.1 Alloys preparation:

The alloys of $Sb_{2(1-x)}Se_{3x}$ were prepared by quenching technique. The exact amount of high purity (99.999%) powders supplied from Merck company (Sb and Se) elements accordance with their atomic percentages (Sb: Se = 0.9:0.1, 0.7:0.3 and 0.5:0.5) were weighted using an electronic balance with the least count of (10^{-4} gm). The mixed elements were sealed in evacuated (~10^{-3} Torr) quartz ampoule (length ~ 25 cm and internal diameter ~ 8 mm). The ampoules containing the elements were heated to (575,550 and 540) ^{o}C for (x=0.1,0.3 and 0.5) respectively for 5 hours depending on the phase diagram then cooled to room temperature. The temperature of the furnace was raised at a rate of 10 ^{o}C/min. During heating the ampoules are constantly rocked. This was done to obtain homogeneous glassy alloys. The amount of elements content of alloys were evaluated by using the equation:

$$W_{Sb2(1-x)Se3x} = W_{Sb\times 2(1-x)} + W_{Se\times 3x} \quad \text{……………..(1)}$$

Where:

W_{Sb} = 121.76 (Atomic weight for Sb)

W_{Se} = 78.96 (Atomic weight for Se)

x = 0.1, 0.3 and 0.5 (concentration of Se)

$Sb_{2(1-x)}Se_{3x}$ powder with high purity (99.999%) pressing it under 5 Ton to form a target with 1.824 cm diameter and 0.441 cm thickness. The target should be as dense and homogenous as possible to ensure a good quality of the deposit.

2.2 Procedure of thin film deposition by PLD:

The pulsed laser deposition experiment is carried out inside a vacuum chamber generally in (10^{-3} mbar) vacuum conditions. The focused Nd:YAG SHG Q-switching laser beam at 500 mJ (pulse width 10 ns, repetition frequency (6Hz) for 500 laser pulse is incident on the target surface making an angle of 45° with it. The substrate is placed in front of the target with its surface parallel to that of the target. Sufficient gap (1.5 cm) is kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam. The films were deposited on glass substrate for different Se contents (x = 0.1, 0.3 and 0.5) at room temperature and different annealing temperatures (373 and 473) K.

2.3 Electrical measurements:

2.3.1 D.C. conductivity measurements:

D.C. electrical conductivity of $Sb_{2(1-x)}Se_{3x}$ thin films which were deposited on the glass substrates, was measured using electrical resistance as a function of temperature within the thermal range (303-473)K, this can be done by putting the film on an electrical oven of the type (Memmert), silver paste was used to fix connection wires on the poles. The resistance of film has been measured by connecting the wires to digital electrometer (Keithely 616). Values of resistance have been measured as a function of temperature. The resistance of the film has been calculated by using the following relation :

$$\rho = R.W.t / L \quad \text{…………………..……..(2)}$$

where :

W: the width of aluminum polar

t : is film thickness (cm)

R : is the resistance
L : is the distance between aluminum poles
Conductivity is the inverse of resistivity:

$\sigma = 1/\rho = L / R.W.t$ ……………………..(3)

The activation energy of all $Sb_{2(1-x)}Se_{3x}$ thin films can be determined by taking the slope of plotting the relationship between (lnσ) as a function of temperature in term of (1000/T).

3.2 Hall effect:

In an attempt to determine Hall coefficient (R_H) type and concentration of the charge carrier and mobility values in $Sb_{2(1-x)}Se_{3x}$ thin films deposited for different Se content (x=0.1, 0.3 and 0.5) at room temperature and different annealing temperatures (373 and 473) K, four poles of aluminum were deposited to study hall effect. When a magnetic field of (0.275 T) intensity is applied vertically to current passing through the film, the electric field is called Hall voltage which is measured by (Keithely 616) . Hall effect could be determined by taking the slope of the plotting relationship between the change of (V_H) as a function of the current pass through the films according the equation :

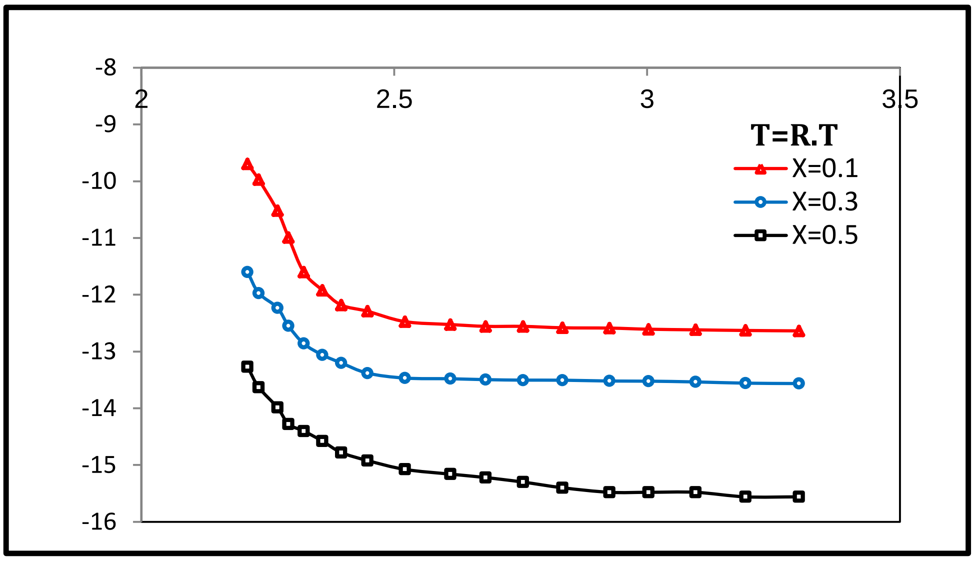
$R_H = Slope. t / B$ ……………………………(4)

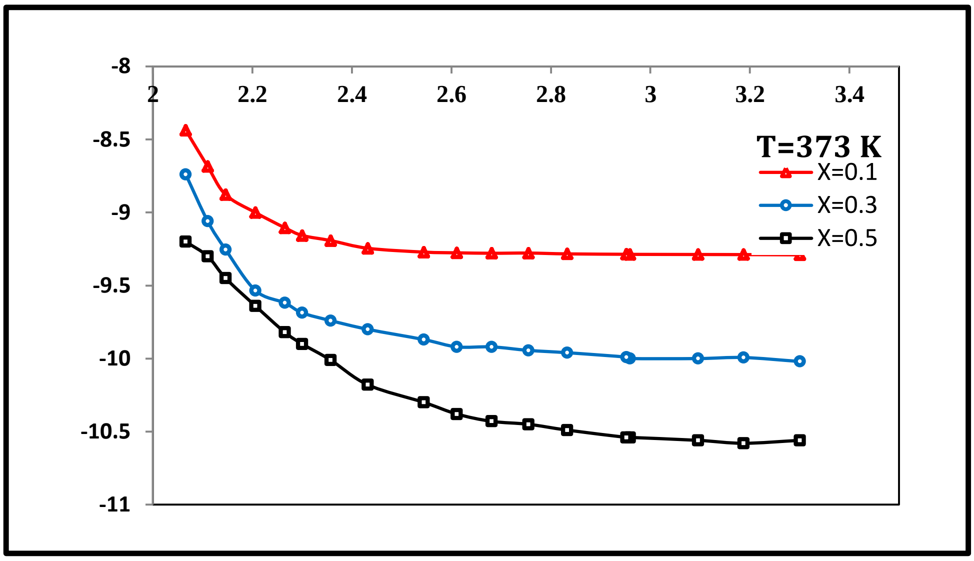
Where:
t = thickness of sample (cm) , B = intensity of the magnetic field (T).

3. Results and discussion

3.1 D.C conductivity:

In order to study the mechanisms of conductivity, it is convenient to plot logarithm of the conductivity (Ln σ) as a function of 1000/T for $Sb_{2(1x)}Se_{3x}$ films with different concentrations of Se (x= 0.1, 0.3 and 0.5) at room temperature and different annealing temperatures (373 and 473) K as shown in figure (1). It is clear from these figures that there are two transport mechanisms, giving rise to two activation energies Ea_1 and Ea_2. At higher temperature range (403-473) K, the conduction mechanism is due to carrier excited into the extended states beyond the mobility edge and at lower temperature range (303-393) K, the conduction mechanism is due to carrier excited into localized states at the edge of the band. It is observed that the activation energies increase while σ_{RT} decreases with increasing of concentration of Se and the activation energies decrease while σ_{RT} increases with increasing of annealing temperatures as represented in the Table (1). This result agrees with [Zayed *et.al*,1995]. The activation energy Ea_1 for $Sb_{2(1-x)}Se_{3x}$ films increases with increasing of concentration of Se, from (1.161 to 0.175) $\times10^{-2}$ eV, from (1.037 to 5.504) $\times10^{-2}$ eV and from (0.202 to 2.888) $\times10^{-2}$ eV when range temperature changes from (303 to 393) K at (x= 0.1, 0.3 and 0.5) respectively, also the activation energy Ea_1 decreases with increasing of annealing temperatures as shown in figure (2), while Ea_2 increases from (0.221 to 0.392) eV, (0.104 to 0.139) eV and (0.081 to 0.123) eV when range temperature changes from (403 to 473) K at (x= 0.1,0.3 and 0.5) respectively, also the activation energy Ea_2 decreases with increasing of annealing temperatures as shown in figure (3). The behavior of E_a with Se concentration and annealing temperature is the same as that for E_g^{opt} . When E_g^{opt} increases, the carriers need high activation energy E_a to transport them from V.B to C.B and vice versa [Qamhieh, *et.al.*, 2007]. From the Table (1) it can also be observed that the activation energy of the first region is less than that of the second region. This can appear in some compounds, where the carrier density could be small enough to give this behavior [Abdel-Satar *et.al.*, 2007]. From figure (4) and Table (1) we can observe that $\sigma_{R.T}$ increases with increasing of annealing temperatures but decreases with increasing of concentration of Se, because of the rearrangement that may occur during annealing temperatures higher which produce an irreversible process in the conductivity [Gheorghiu and Theye (1981)].





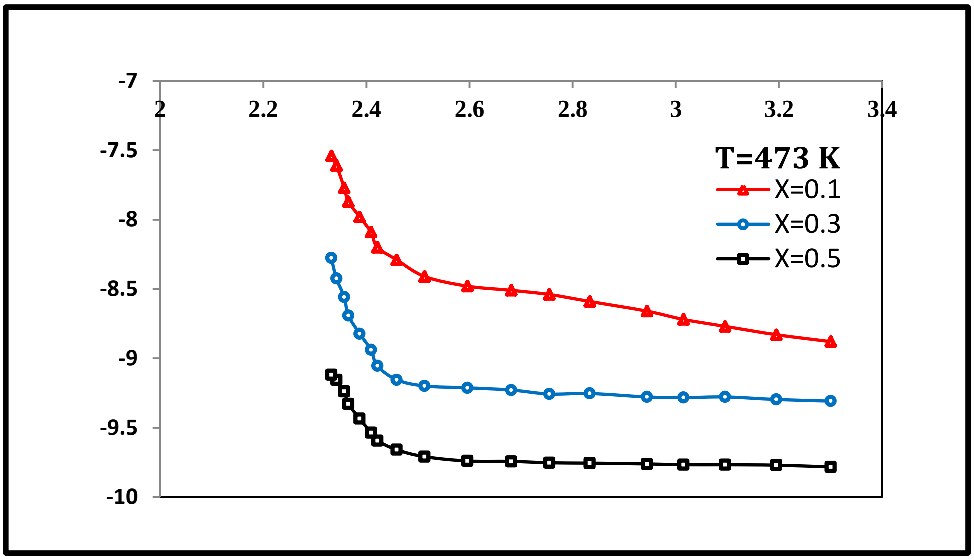


Figure (1): The relation between Ln (σ) versus reciprocal of temperature for $Sb_{2(1-x)}Se_{3x}$ films with different concentration of Se and different annealing temperatures.

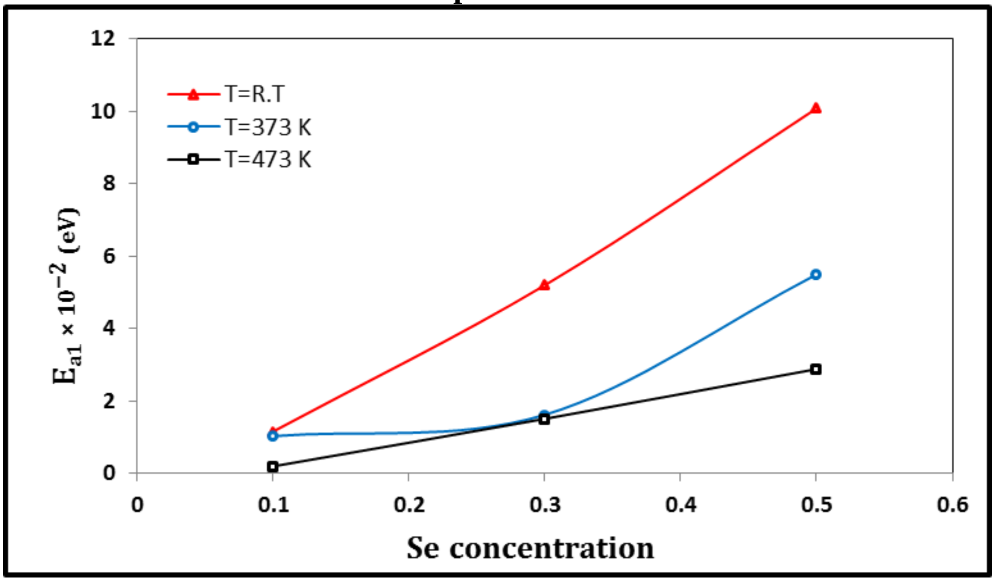


Figure (2): The variation of the activation energy Ea_1 for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se and different annealing temperatures.

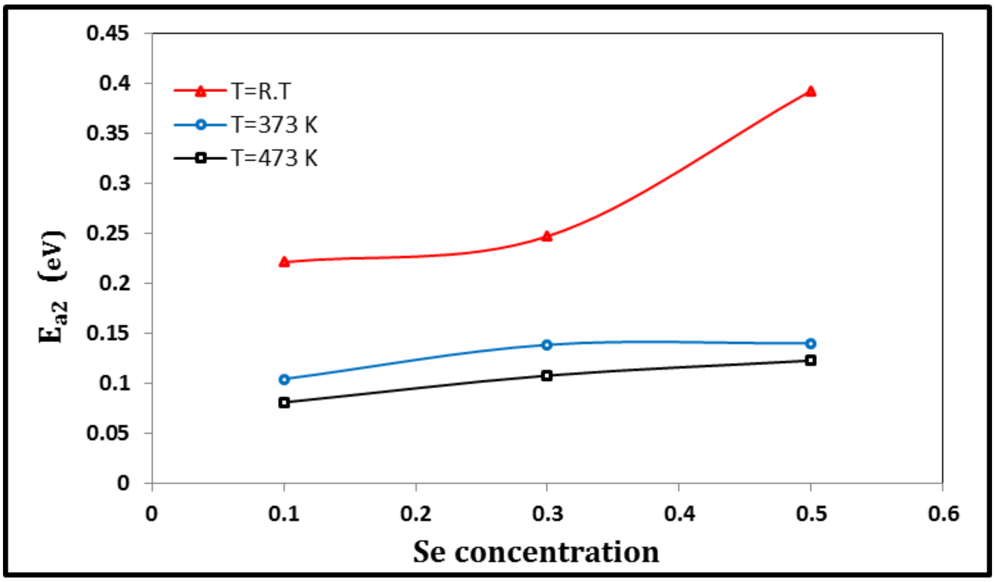


Figure (3): The variation of The activation energy Ea_2 for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se and different annealing temperatures.

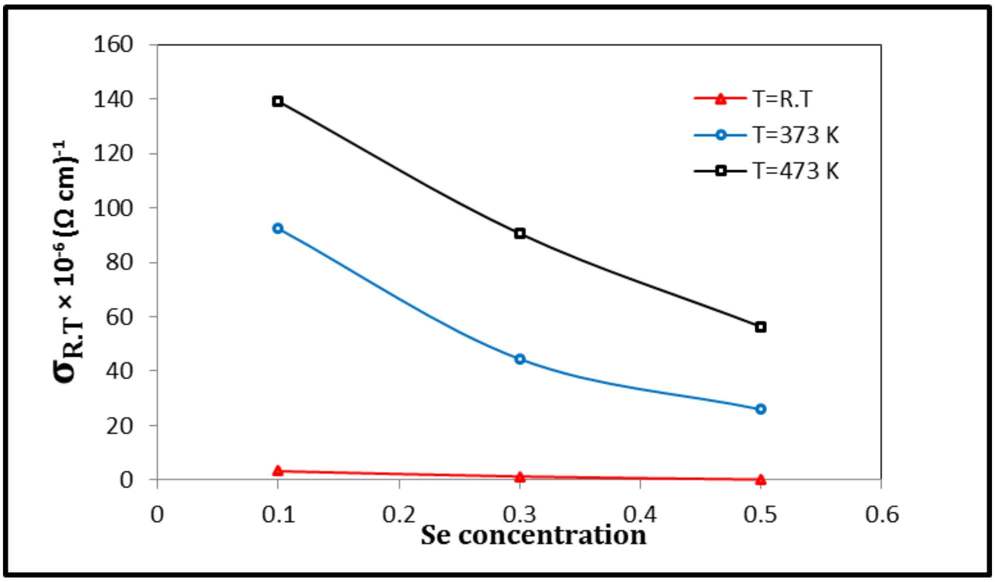


Figure (4): The variation of conductivity $\sigma_{R.T}$ for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se and different annealing temperatures.

Table (1): The values of E_{a1} and E_{a2} and these ranges for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se (x) and different annealing temperatures.

Ta (K)	x	$\sigma_{R.T}\times10^{-6}$ $(\Omega\ cm)^{-1}$	$E_{a1}\times10^{-2}$ (eV)	Range Temp.(K)	E_{a2} (eV)	Range Temp.(K)
R.T	0.1	3.25181	1.160925	303-393	0.22113	403-473
	0.3	1.28571	5.2026	303-393	0.24691	403-473
	0.5	0.17473	10.0878	303-393	0.39238	403-473
373	0.1	92.36153	1.03673	303-393	0.10429	403-473
	0.3	44.50095	1.62324	303-393	0.13849	403-473
	0.5	25.93285	5.50361	303-393	0.13993	403-473
473	0.1	139.14417	0.20183	303-393	0.08093	403-473
	0.3	90.60511	1.51369	303-393	0.10773	403-473
	0.5	56.34596	2.88765	303-393	0.12269	403-473

3-2 Hall effect:

The type of charge carriers, concentration (n_H) and Hall mobility (μ_H), have been estimated from Hall measurements. Table (2) shows the main parameters estimated from Hall effect measurements for $Sb_{2(1-x)}Se_{3x}$ thin films deposited with different concentrations of Se at room temperature and different annealing temperatures (373 and

473) K. We can notice from this table that the films have a positive Hall coefficient. This means that the type conducting (p–type charge carriers), This results is in agreement with [Zayed *et.al*, (1995)], [Kang *et.al*, (2007)], [Yanqing Lai *et.al*, (2012)] and [Yanqing Lai *et.al*, (2012)]. Also we can notice from table (2) and figures (5) and (6) respectively, that the carrier's concentration (n_H) increases with increasing of concentration of Se, while Hall mobility (μ_H) decreases with increasing of concentration of Se. The conductivity (σ) decreases with increasing of concentration of Se as shown in figure (7). Also the carrier's concentration (n_H) decreases with the increasing of annealing temperatures, while the Hall mobility (μ_H) increases with the increasing of annealing temperatures, this may be due to the decrease in defects inside the energy gap and to the transformation to crystalline structure. It can be seen that the carrier mobility increases with decreasing the carrier concentration which is due to the increase in concentration of Se and vice versa. The conductivity (σ) increases with increasing of annealing temperatures. The increase of the density of charge carrier's is essentially because of the lowering the potential barrier. While the decreasing of mobility results from the inverse relation between (μ_H) and (n_H). These results are in agreement with [Kang *et.al*, (2007)].

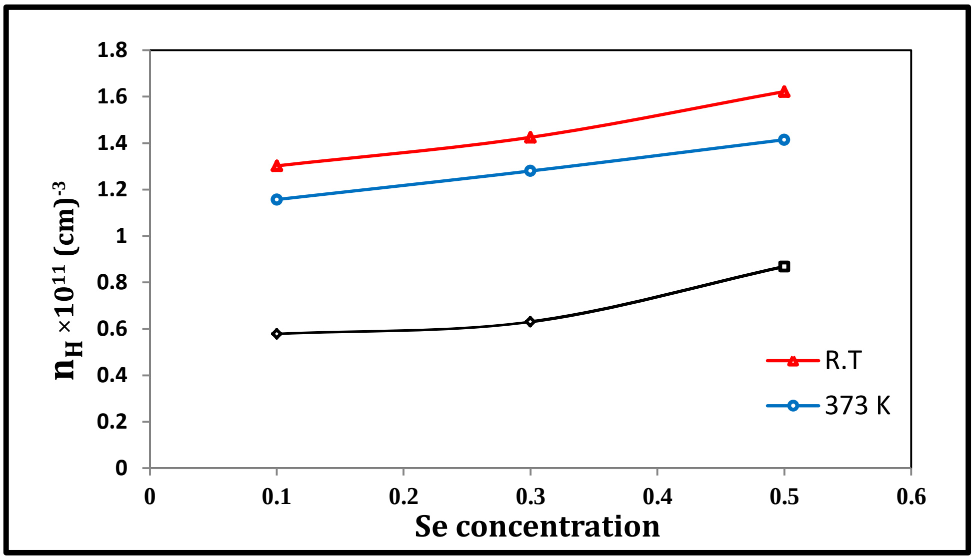


Figure (5): The variation of carrier concentration for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se and different annealing temperatures.

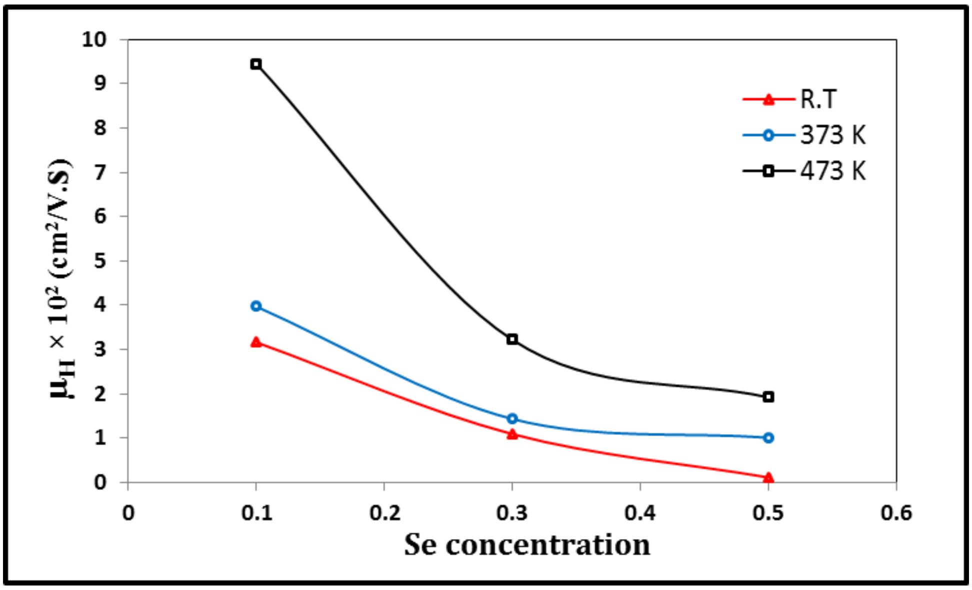


Figure (6): The variation of mobility for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se and different annealing temperatures.

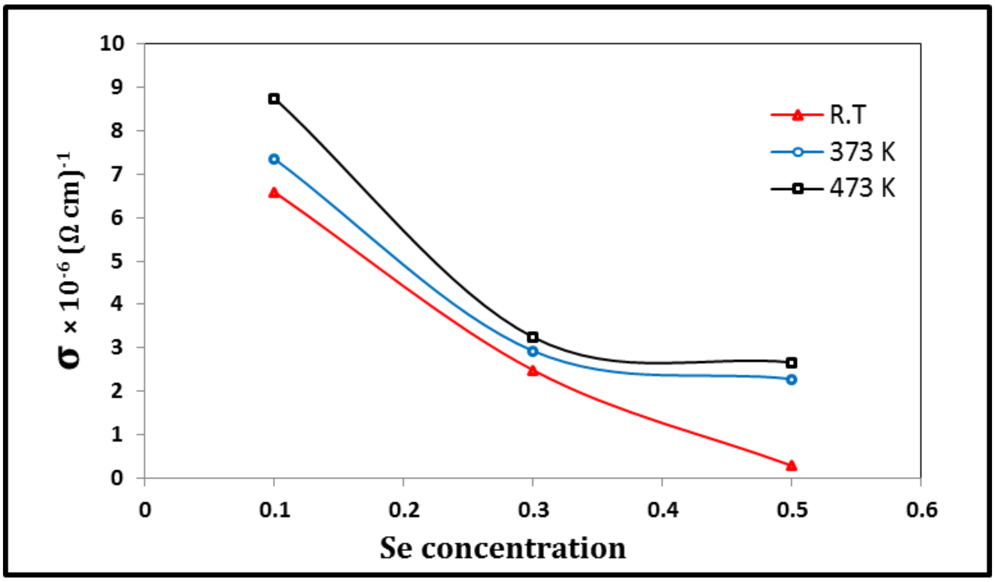


Figure (7): The variation of conductivity for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se and different annealing temperature.

Table (2):Hall effect measurements for $Sb_{2(1-x)}Se_{3x}$ films with different concentrations of Se and different annealing temperature.

Ta (K)	x	$n_H \times 10^{11}$ $(cm)^{-3}$	$R_H \times 10^{7}$ (cm^3/C)	$\mu_H \times 10^{2}$ $(cm^2/V.s)$	$\sigma \times 10^{-6}$ $(\Omega.cm)^{-1}$
R.T	0.1	1.3021	4.799	3.16	6.585
	0.3	1.425	4.3859	1.092	2.4898

	0.5	1.622	3.8533	0.113	0.29326
373	0.1	1.157	5.4019	3.97	7.3493
	0.3	1.28	4.8828	1.432	2.93274
	0.5	1.4146	4.4182	1.01	2.28599
473	0.1	0.5783	10.8075	9.45	8.74393
	0.3	0.6306	9.91119	3.22	3.24885
	0.5	0.8686	7.195487	1.92	2.66834

4. Conclusions

There are two activation energies for $Sb_{2(1-x)}Se_{3x}$ thin films ,the activation energies increase while σ_{RT} decreases with increasing of Se concentration and the activation energies decrease while σ_{RT} increases with increasing of annealing temperature. $Sb_{2(1-x)}Se_{3x}$ thin films have a positive Hall coefficient (p–type charge carriers), concentration of charge carriers n_H increases with increasing concentration of Se, also charge carriers n_H decrease with increasing of annealing temperatures, while the mobility μ_H and the conductivity (σ) showed opposite behavior.

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