

γ -radiation Effect on Some Electrical Properties and Optical Energy Gap of a - Ge_{1-x}Sb_x Thin Films

تأثير أشعة كاما على بعض الخواص الكهربائية وفجوة الطاقة البصرية لأغشية a - Ge_{1-x}Sb_x الرقيقة

عبد الله سعيد عاشور – قسم الفيزياء /كلية العلوم /جامعة ذمار / اليمن
فيصل علي مصطفى – قسم فيزياء الليزر /كلية العلوم للبنات/ جامعة بابل
إكرام عطا عجاج – قسم الفيزياء/كلية العلوم/جامعة بغداد

ABSTRACT

The a-Ge_{1-x}Sb_x thin films of (250±20) nm thickness were fabricated according to the weight percentages (x = 0.5, 1, 1.5, 2)%wt, by using the thermal evaporation technique under vacuum (10⁻⁶mbar) and (2.7±0.05)A^o/s. The specimens have been exposed to(500rad) γ -ray. The D.C. electrical measurement were carried out in a range of 0 -3Vol. The effect of γ -radiation on Hall parameters and optical energy gap were investigated for determining the no. of carriers and controlling on optical energy gap of semiconductors. The examination x-ray diffraction showed that all the films have amorphous nature. There are two activation energies for all films of n-type at (493-305)K that the carriers increase to (41.67 x 10¹⁹ cm⁻³)by increasing the percent to x=2,and they showed a decrease after exposed to radiation to(29.76 x 10¹⁹ cm⁻³) at the same value of x. But the mobility decrease to (0.140 x 10⁻³ cm²/V.s)by increasing of x to 2 percentage and they are increasing after exposure to γ - rays with (0.170 x 10⁻³ cm²/V.s). The optical energy gap is (0.840eV) for a-Ge(unexposed to γ -rays), but becomes (0.872eV) after exposure , but it is increasing from (0.786eV) to (0.815eV)after exposed to radiation at x=2. This indicates an absorption edge shift towards high energies due to the effect of radiation.

KEYWORDS: amorphous thin films, γ - rays, germanium doping, antimony, Hall phenomena , optical band gap, GeSb.

الخلاصة:

حضرت أغشية الجرمانيوم النقية والمطعمة بالانتيمون (a - Ge_{1-x}Sb_x) في ضوء النسبة الوزنية (x=0.5, 1, 1.5, 2)% wt باستخدام تقنية التبخير الحراري تحت تفريغ ضغط 10⁻⁶ Torr ، ثم عرضت النماذج الى جرعة 500 rad من أشعة كاما وفحصت بحيود الأشعة السينية قبل التشعيع وبعده وتبين أنها ذات طبيعة عشوائية، وان لجميع الأغشية المحضرة طاقتي تنشيط عند درجة حرارة (493-305)K ، وأنها نوع n وتركيز حاملات الشحنة قد ازداد الى قيمة (41.67 x 10¹⁹ cm⁻³) بزيادة نسبة التطعيم الى 2% ، ونقل بعد التعرض للإشعاع الى قيمة (29.76 x 10¹⁹ cm⁻³)، لكن التحركية قد قلت الى قيمة 0.140 x 10⁻³ cm²/V.s بزيادة النسبة الى 2 لكنها تزداد بعد التعرض للإشعاع الى قيمة (0.170 x 10⁻³ cm²/V.s) . أما قيمة فجوة الطاقة البصرية لغشاء الجرمانيوم النقي العشوائي فكانت (0.840eV) وأصبحت (0.872)eV بعد التعرض للإشعاع. لكنها تزداد من قيمة (0.786eV) الى قيمة (0.815eV) عند النسبة 2 = x ، وهذا يعني انحراف حافات فجوة الطاقة نحو قيمة الطاقة العليا.

1- INTRODUCTION

The a - semiconductor has unappeared peaks in x-ray diffraction technique as result of no arrangement of crystal planes ^[1]. The addition of antimony atoms to germanium atoms leads to form covalent bonds with germanium atoms, whenever have generated dangling bonds, the fifth electron has produced energy level (E_d) positioned directly under condition band inner energy gap called doner level ^[2]. The most generated defects from radiation is point defects ^[3]. The effect of radiation damage was related with Frenkel defects^[4]. The clustering of point defect has reached to supersaturation or where they are meeting two or more than of point defects during its movement and assembled around them ^[5, 6]. The amorphous case can obtained by quenching and condensed material from vapor^[7]. The amorphous semiconductor contains high density of energy levels produced by structural defects that appear in three regions^[8]. There are approach in absorption between crystalline and amorphous ,the difference is in cut-of frequency that is less in amorphous^[9]. The interaction with radiation have generated to pair of (hole ,electron) displaced of atom from its site ,and so formed the secondary defects and free migration of primary defect^[10]. (Koc. Et al., 1972) ^[11] was prepared amorphous germanium film that produced the

conductivity gradually decreased with increasing annealing temperature to the crystalline temperature after that it was absorbed, so the conductivity increase in high values, but d.c. conductivity of film resulted from hoping beside energy Fermi level observed by (Kontek, et al. 1973)^[12]. This conductivity decrease by thermal annealing of films prepared by thermal evaporation to (450K) as found by (Seager et al., 1974)^[13]. The Hall mobility was less than ($10^{-3} \text{ cm}^2/\text{V.s}$), while it was observed that the conductivity decrease as the measured time was after deposition for a long time, (Theye., et al. 1980)^[14]. The doping by boron and phosphor on (a-Ge: H) lift the conductivity values while activation energy decrease (Haushildt, et al. 1982)^[15]. Also Fermi energy level was shifted along mobility edge, the doping by ion implantation of two material as prepared by (Khoklov, at al. 1984)^[16] increase the conductivity from $10^{-3} (\Omega.\text{cm})^{-1}$ to $10^{-1} (\Omega.\text{cm})^{-1}$, since the doping dose has increased from (10^{14} cm^{-2}) to (10^{17} cm^{-2}). (Srivastava et al. 1986)^[17] has irradiated specimens of (a-Ge) films prepared by thermal evaporation in vacuum with laser which the effect was similar of thermal annealing of d.c. conductivity. The type of affected radiation on films have given low or high value of conductivity. (Anderson et al., 1974)^[18] concludes that the absorption edge deflect to low energies, when a-Ge is doped with boron. The electronic transitions and its effect of doping and hydrogentic which leads to improvement the (a-Ge: H) doping with phosphor and boron was observed by (Hamadi, 1999)^[19]. (Jordana Bandaru, 2002)^[20] study Influence of the Sb dopant distribution on far infrared photoconductivity in Ge:Sb blocked impurity band detector and find that extended long wavelength response which increases with bias has been observed in Ge:Sb BIB detectors. A significant Sb concentration gradient in the transition region between the blocking layer and active layer was observed using SIMS (M. Hayes et al., 2008)^[21] have been prepared gold metal films having thicknesses of 30 and 100 nm by means of thermal evaporation on bulk-grown (111) n-type germanium doped with Sb to a level of $2.5 \times 10^{15} \text{ cm}^{-3}$. (X.H.Han, et al. 1998)^[22] were deposited nanometer Ge particle (NGP) embedded Si oxide films on p-type Si substrates using the rf magnetron sputtering technique with a Ge-SiO₂ composite target. (T. Trisawa, 2002)^[23] have obtained ultrahigh room-temperature (RT) hole Hall and effective mobility in Si_{0.3}Ge_{0.7}/Ge/Si_{0.3}Ge_{0.7} heterostructures with very small parallel conduction. The aim of the paper is to report the determination in both no. of negative carriers & optical energy gap of a-Sb doped Ge films under the influence of γ -irradiation and suitability of these devices for photocell, solar cell and other electronic devices.

2-THEORY

(a) The change of electrical conductivity(σ) with absolute temperature(T) obeys the relation^[24]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{K_B T}\right) \quad (2-1)$$

Such that E_a is an activation energy (Joule), T absolute temperature (K), K_B is a Boltzmann constant ($1.3806 \times 10^{-23} \text{ J/K}$), σ_0 the conductivity at zero absolute temperature ($\Omega.\text{cm}$)⁻¹.

At high temperature, the conductivity process occurs during excitation of the charge carriers at extended levels above mobility edge of covalent band with respect of negative carriers^[24].

When the magnetic field (B_z) has perpendicular exposed on semiconductor films contains electric current, the Hall voltage will generate in transverse direction or the charge carriers has deflected with action of effective magnetic field.

The type and concentration of these generated carriers in volume unit are from:

$$R_H = -\frac{f}{ne} (\text{cm}^3 / \text{columb}) \quad (2-2)$$

Where f is the scattering factor $\cong 1$, n is concentration of charge carriers and the negative sign represents the n-type carrier.

Also the Hall mobility is calculated from^[25]:

$$\mu_H = |R_H| \sigma_{R.T.} \quad (2-3)$$

Where $\sigma_{R.T.}$ is the d.c. Conductivity at room temperature.

(b) The optical absorption occurs in a-semiconductors as a result of electron transition from low level to high level by excitation of enough photon energy(17) and occur quick increase in photon absorption when there equal to forbidden gap, the absorption coefficient in amorphous semiconductor is given by^[8]:

$$(2-4) \quad \alpha h\nu = \beta(h\nu - E_g^{opt.})^r$$

Where β is constant inversely proportional with degree of amorphous as function to incident photon energy material, and r is depend on electronic transformation in semiconductor^[25]. The transfer occurs in direct($k_i=k_f$), and in an indirect ($k_i \neq k_f$) or the momentum is non- conservation .From relation (2-4) the absorption region is high $\alpha \geq 10^4 \text{ cm}^{-1}$ that occurs when the charge carriers transferred from extended level in valence band to conduction band. The exponential absorption is between $1 \text{ cm}^{-1} < \alpha < 10^4 \text{ cm}^{-1}$, the relation is given by^[24]:

$$\alpha = \alpha_0 \exp\left(-\frac{h\nu}{\Delta E_e}\right) \quad (2-5)$$

Is the absorption coefficient, α

α

is constant proportionality, and ΔE_e is the width of tails. α_0

α_0

The weak absorption region is very little ($\alpha < 1 \text{ cm}^{-1}$), which represents the electronic transitions at localized tail levels inside the mobility gap and obeys the equation:

$$\alpha \approx \alpha_{01} \exp\{h\nu/\Delta E_{el}\} \quad (2-6)$$

Such that $\Delta E_{el} > \Delta E_e$ so that depend on the nature of material and preparation conditions. α_{01} is the principal absorption coefficient.

3- EXPERIMENTAL

a. Preparation of films: The two boats (Tungsten and Molybdenum) were used to deposit the aluminum electrodes (Edward E 12E2 system) and $\text{Ge}_{1-x}\text{Sb}_x$ of ($x = 0, 0.5, 1, 1.5, 2$) %wt. (Edward E603A system) respectively.

The aluminum etching masks were correctly placing on glass substrates with $(7.6 \times 2.6 \times 0.06) \text{ cm}^3$ dimensions. The distance between the two boats are (16 cm). The doping process are carried out by thermal diffusion at (373 – 473)K with average deposition ($2.7 \text{ \AA} / \text{s} \pm 0.05$) for one hour under low pressure (4×10^{-6} torr). The thickness measurements (350nm) are carried out by relation^[26]:

$$t = \frac{m}{2\pi R^2 \rho} \quad (3-1)$$

Where R is the distance between boats and substrates (cm), ρ the density of evaporated material (gm/cm^3). Also the optical method related to light interference are used:

$$t = \frac{\lambda \Delta x}{2 x} \quad (3-2)$$

Where λ is the wavelength of sodium source (5893 \AA).

b. Structural examinations: The samples were examined by using x-ray diffraction (Philips Diferactometer) ($1.541 \text{ \AA} - \text{Cu}$) wavelength at $(20-60)^\circ$.

c. Activation energy: The two activation energy are calculated by putting the samples in thermal oven, taking the passing current in specimens as a function of temperature ranges (305-493)K with the relation^[24]:

$$\ln \sigma = \ln \sigma_o - \frac{E_a}{K_B T} \quad (3-3)$$

d. Hall parameters: The effective constant magnetic field ($B_z = 0.257$ Tesla) on samples are generated Hall voltage, the Hall coefficient was calculated from:^[24]

$$R_H = \left(\frac{V_H}{I} \right) \left(\frac{t}{B_z} \right) \left(\frac{cm^3}{C} \right) \quad (3-4)$$

Where t is the thickness of the films.

So the concentration of charge carriers could calculated from equation (2-2) and mobility from (2-3).

e.The an absorbance and optical energy gap: To calculate the E_p^{opt} (Lambda-9UV/VIS/NIR Spectrometer) is used to measure the absorbance as a function to wavelength (850-1200) nm, and calculate the photon energy from the equation:

$$E = \frac{1240}{\lambda(nm)} (eV) \quad (3-5)$$

The absorption coefficient is calculated by the equation[:

$$\alpha = \frac{2.303}{t} A(cm^{-1}) \quad (3-6)$$

Where A is the absorbance

f. The irradiation of films: The exposed of specimens to γ -ray is (500rad) doses emitted from Co^{60} at rate (0.59Mrad/hr.) with energy (1.25MeV) that placed at (10cm) from radiated source for (50sec) by using the equation^[26]:

$$D_t = D_o \exp(-\lambda_a t_o) \quad (3-7)$$

Where D_o is average dose of radiated source at manufacture, t_o the history of making, λ_a is the disintegration constant.

4- RESULTS

a.Effect of γ -Rays on the Structural Examinations of a- $Ge_{1-x}Sb_x$ thin film specimens:

The structural examination showed that the films have amorphous nature before and after γ -radiation for all doping films as illustrated in Figures 1 and 2.The schematic description of generation of vacancies and gangling bonds as a result to radiation was shown in Figure 3.

b. Effect of γ -Rays on Activation Energies and Hall parameters:

The d.c. conductivity at room temperature increases with increasing doping and decreases after irradiation. The variation percentages indicate that the value $\sigma_{R.T.}$ decrease after irradiation of value 10.2% of pure germanium films, but decreasing with different ratios of doping specimens, also the first and second values of activation energy decrease with increasing doping and has high value after exposure to radiation as illustrated in Figures 4 and 5.

The results show that Hall voltage is inversely proportional with passing current at room temperature as shown in Figures 6, 7, 8, 9, and 10.

The density concentration of carriers increases with increasing of doping percentages and decreases after irradiation. Also the Hall mobility decreases as doping increase and increase after irradiation .

The variation ratios of Hall parameters(R_H , n , μ_H) before and after exposure are shown in table 1 such that the negative carriers is different of doping films. The negativity of Hall coefficients decrease with increasing doping percentages. The R_H and μ_H increase after irradiation but the carriers no. (n) decrease after exposed to radiation.

c. Effect of γ -Rays on optical energy gap:

The increasing in absorption coefficient as photon energy increase in percent ($x = 0,0.5,1,1.5,2$)wt% thin film, while the absorption edges shifted to high energy after exposure to radiation. It was observed that optical energy gap is decreasing when the doping increases, but decreases after exposure to radiation as shown in Figure 11.

5- DISCUSSION

a. The $a\text{-Ge}_{1-x}\text{Sb}_x$ films remain with amorphous structure after exposed to radiation because of the generated different surface bulk defects as a result to radiation, in addition to more dangling bonds.

b. It is observed that the d.c. conductivity of thin films increased as increasing in doping percentages because of increasing of donor levels below conduction band. The contribution of charge carrier concentration in conduction is high. The required energy to transfer electron between two edges of bands decrease with increasing dopant percentages, because of a abundance carriers which leads the carrier transformation between two edges at low energies (Hauschildt, et al., 1983) ^[12]. The effect of radiation to decrease of d.c. conductivity attributed to the high energy photons which decreasing the donors levels because of generated of pairs(vacancy-donor atom) which related the transfer of negative carriers between two edges. The clustering of point defects in amorphous structure that resist the movement of negative carriers, also increase in two activation energies.

c. The decreasing of mobility when the concentration of charge carriers increase leads to the probability of collision increase. The irradiation refers to the contraction of charge carriers because of created defects or vacancies in amorphous structure, which trapped doner centers that decreasing of carriers contribution. Whenever occurrence irregular atomic displacements in amorphous networks. The excess vacancies is generated as a result of absorption of gamma ray. But the increasing of mobility after irradiation is attributed to generation of defects that retard the electron movements inner film..

6- CONCLUSIONS

The structural, Hall parameters and optical bands were investigated before and after exposure to γ -rays, to explore the possibility of their use in semiconductor devices. The d.c. conductivity is increasing to three times at (2% wt), and decreased by radiation. The activation energy, Hall mobility are decreasing by doping and increasing by irradiation. So it could control on conductivity (activation energy) and the carrier numbers of semiconductor devices by radiation dose or to vary optical energy gap according to requirements in light of boundary values.

It was observed that the doping of Ge with Sb shifted the optical absorption edges to low energies, and so occur decreasing in optical band gap, this attributes the increasing of doping percentages and leads to generate number of donor levels under conduction band , and so to reduce the required energy to transfer the contributed electron to conduction process.

REFERENCES

- [1]C.A. Hogarth & L.A. Wright "Proceeding of International Conference of Physics of Semiconductors" Moscow, P. 213 (1969).
- [2]Blakemore, (Solid state physics),3rd ed. (1983).
- [3]S.M. Sze "Physics of Semiconductors devices" 2nd Ed. By N.Y. John Wiley & Sons, Inc. (1981).
- [4]C. Kittel "Introduction to solid State Physics" 5th Ed., John Wiley & Sons, Inc. (1996).
- [5]W. James Corbett" Electron radiation in semiconductor and Metals", New York and London(1966).
- [6]G. Dearnaly & D.C, Northrop "Semiconductor counters for Nuclear Radiation" 2nd Ed. London (1996).

- [7]Ints. Physics Conf. Ser. No. 16 “Radiation damage and defect in semiconductor” London & Bristol (1972).
- [8] W. James, Corbett “Electron radiation in Semiconductor and Metals” New York and London (1966).
- [9]J. Taus , “Amorphous & Liquid Semiconductor” London, plenum,(1974).
- [10]J. Taus and Menth, “State in the Gap” J. of Non-crystalline Solids, Vol. (8-10) P. 569. (1972).
- [11]S. Koc, M. Zavetova & J. Zemek, “Thin Solid Films”. Vol. 10, P (165) (1972).
- [12]M.L. Knotek, M. Pollak & T.M. Danavan Physical Review Letter” Vol. 3, No. 18, P. 853 (1973).
- [13]G.H. Seger, A.H Clark, M.L. Knotek “Amorphous & Liquid Semiconductors” Ed. By J. Stake & W. Berring london P. 1133 (1974).
- [14]M.L. Theye, A. Gheorghiu & M. Gandais, “J. Non. Crys. Solids”, Vol. 37, (P. 301) (1980).
- [15]D. Hauschildt, M. Stutzmann, J. Stuke, & H. Dersch, “Solar Energy Materials” Vol. 8, No. 3, P. 319 (1983).
- [16]A.F. Khokholvo, A.V. Ershov, & A.L. Mashin, “Sov. Phys. Semi.” Vol. 18, No. 9, P. 1003 (1984).
- [17]G.P. Srivastava, K.N. Tripathi, N.K. Seghal, “J. of Materials Sciencs”, Vol. 21, P. 2972 (1986).
- [18]G.W.Anderson,J.E.Davey,J.Comes,N.Sakes&W.H.Luck"J.Appl.Physics"Vol.45,No.10, P.4528,(1974).
- [19]Hamadi “Study of Optical Absorption and electronic Transition of (a-Ge: H, a-Ge) of doped films, College of Science-Baghdad University, Ph.D. Thesis 1999.
- [20]Jordana Bandaru Jeffrey W. Beeman Eugene E. Haller Stacy Samperi Nancy M. Haegel<http://repositories.cdlib.org/lbnl/LBNL-49589>(University of California) Year Paper LBNL-49589,(2002).
- [21]M. Hayes¹, F. Schrepel², S.M.M. Coelho¹, F.D. Auret¹, J.M. Nell¹ and W Wesch². Journal of Physics: Conference Series 100 042005 IOP Publishing,(2008).
- [22]H. X. Han, Z. P. Wang, and G. H. Lij, Appl. Phy. ”Condensed Matter :Dielectric and Optical Propertes” / Volume 84 / Issue 1 /1998 .
- [23]T. Trisawa S. Tokumitsu and T. HattoriK. Nakagawa "Electronic transport and semiconductors" ,Appl. Phys. Lett. /Volume 81 / Issue 5 / (2002) .
- [24]R.A.Smith,”Semiconductors”,2nd,Ed.(1978).
- [25]M.A.Omer”Elementry Solid State Physics& Application”Addison-Weily,Publishing Company,Inc.(1975).
- [26] F.A.Al-Bassam,(Effect of Alpha and Beta Particles on Pure and Doped Germanium Films”, Ph.D., Thesis, Univ. of Baghdad,(1996).

FIGURE CAPTIONS

Figure 1. Schematic diagram of amorphous X- ray diffraction of pure and doped Ge with Sb thin films at x=(0,0.5,1,1.5,2)wt% before exposed to gamma radiation.

Figure 2. Schematic diagram of amorphous X- ray diffraction of pure and doped Ge with Sb thin films at x=(0,0.5,1,1.5,2)wt% after exposed to gamma radiation.

Figure 3. Schematic diagram of the generation of vacancies and dangling bonds in an amorphous structure of Sb doped Ge thin films as a result of radiation.

Figure 4. First activation energy vs. percentage concentration for an Sb doped Ge thin films at 27 °C, before and after exposed to gamma radiation.

Figure 5. Second activation energy vs. percentage concentration for an Sb doped Ge thin films at 27 °C, before and after exposed to gamma radiation

Figure 6. Hall voltage factor vs. the transferred current for a-pure Ge thin films at 27 °C, the slope represents the intrinsic Hall resistance before and after exposed to gamma radiation.

Figure 7. Hall voltage factor vs. the transferred current for an Sb doped Ge thin films at 27 °C, before and after exposed to gamma radiation at x=0.5.

Figure 8. Hall voltage factor vs current for the transferred current an Sb doped Ge thin films at 27 °C, before and after exposed to gamma radiation at x=1

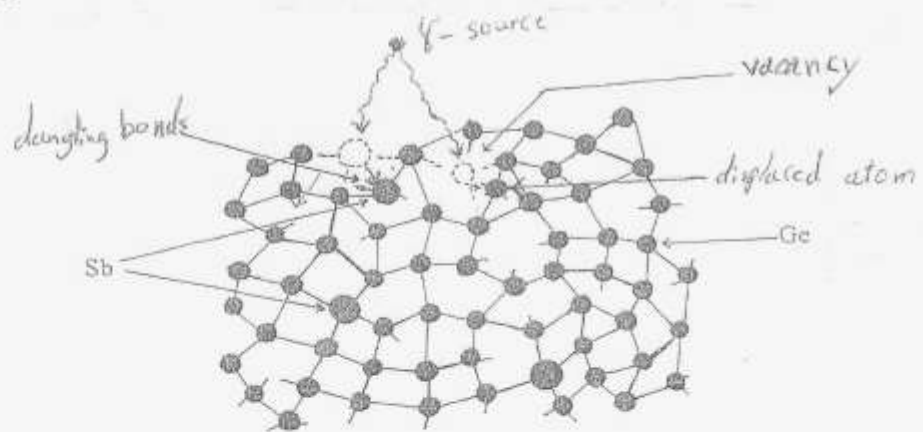
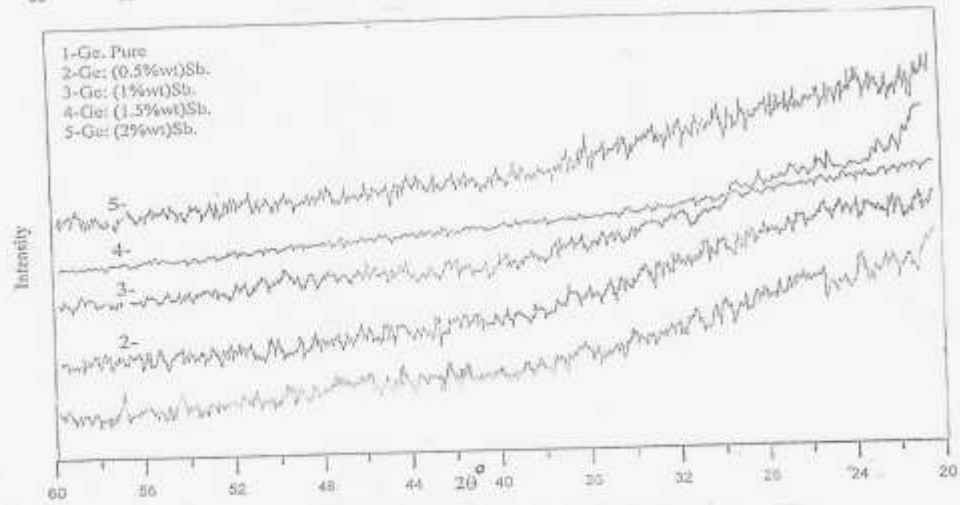
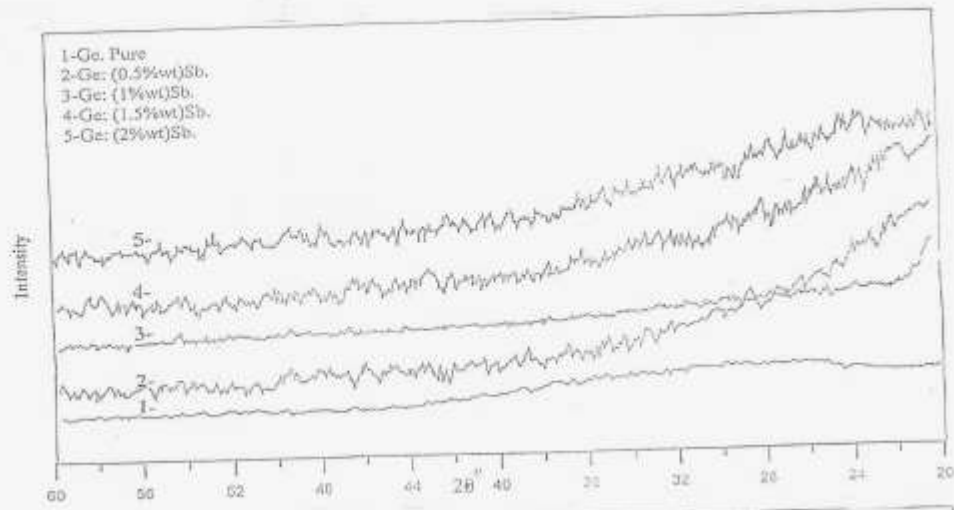
Figure 9. Hall voltage factor vs. current the transferred for an Sb doped Ge thin films at 27 °C, before and after exposed to gamma radiation at x=1.5.

Figure 10. Hall voltage factor vs. the transferred current for an Sb doped Ge thin films at 27 °C, before and after exposed to gamma radiation at x=2.

Figure 11. Optical energy gap of n-type vs. percent concentration of an Sb doped Ge thin films at 27 °C, before and after exposed to gamma radiation at (x=0,0.5,1,1.5,2)wt%.

Table 1. The variation percentages of R_H , n and μ_H before and after exposure to gamma radiation

Doping percentages wt%	$-R_H$ (cm ³ /C)			$n \times 10^{19}$ (cm ³)			$\mu_H \times 10^{-3}$ (cm ² /V.s)		
	before	after	Variation percentages	before	after	Variation percentages	before	after	Variation percentages
0	0.104	0.124	19.23	6.009	5.040	-16.13	0.328	0.351	7.01
0.5	0.069	0.092	33.33	9.058	6.763	-25.34	0.293	0.340	16.04
1	0.029	0.040	37.93	21.551	15.625	-27.49	0.169	0.208	23.07
1.5	0.021	0.030	42.86	29.762	20.833	-30.00	0.143	0.184	28.67
2	0.015	0.020	33.33	41.667	29.762	-28.57	0.140	0.170	21.43



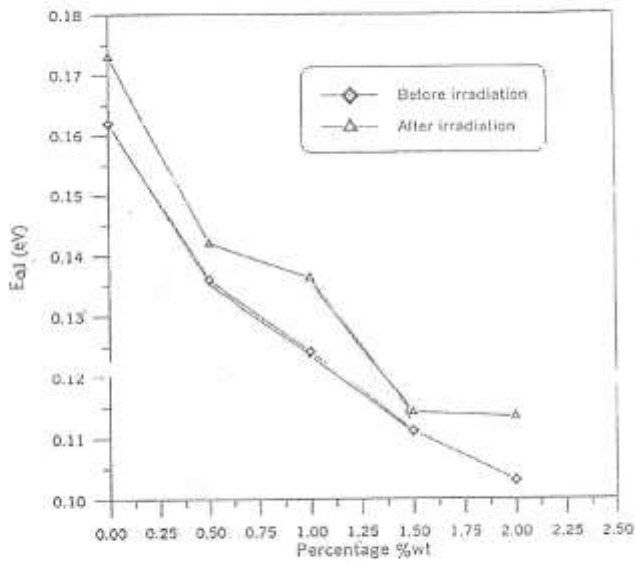


Fig.4

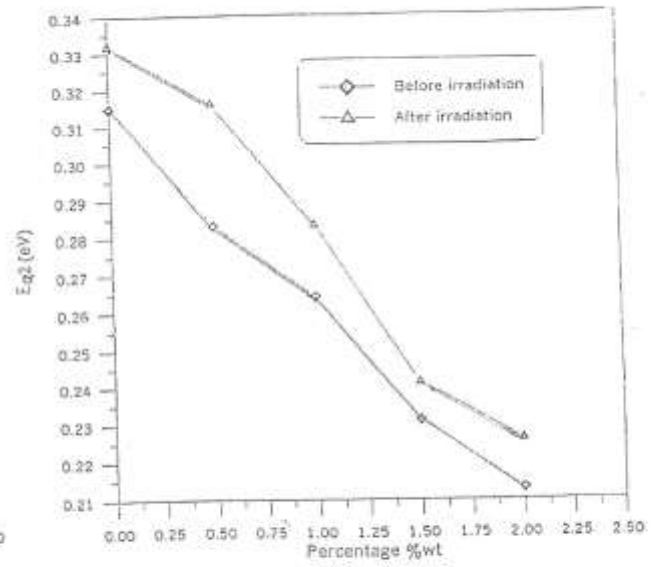


Fig.5

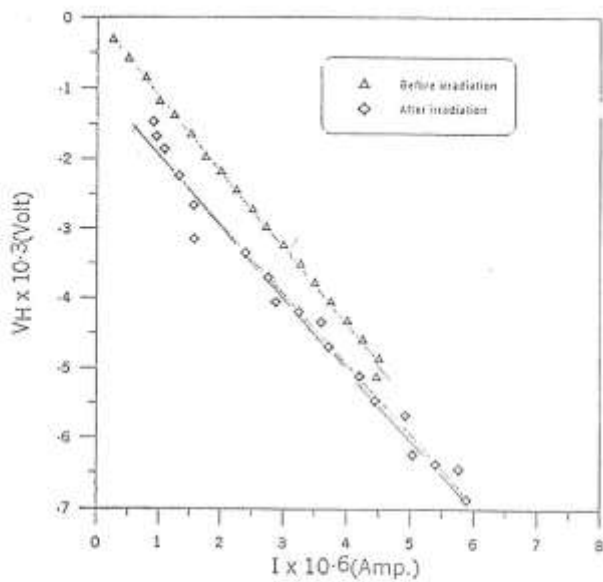


Fig.6

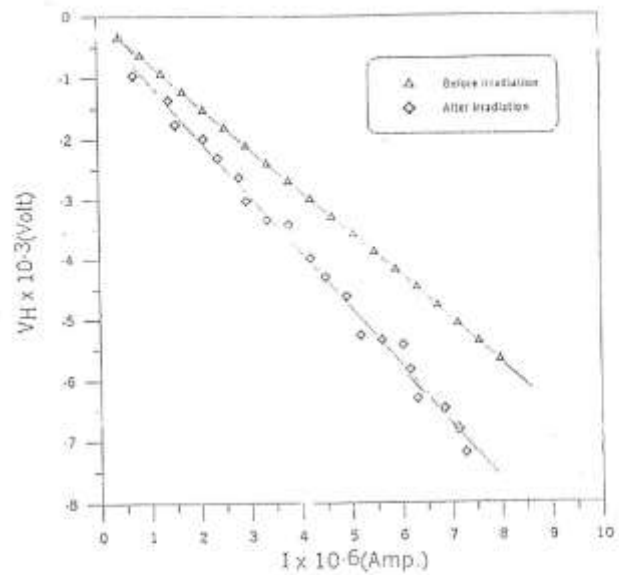


Fig.7

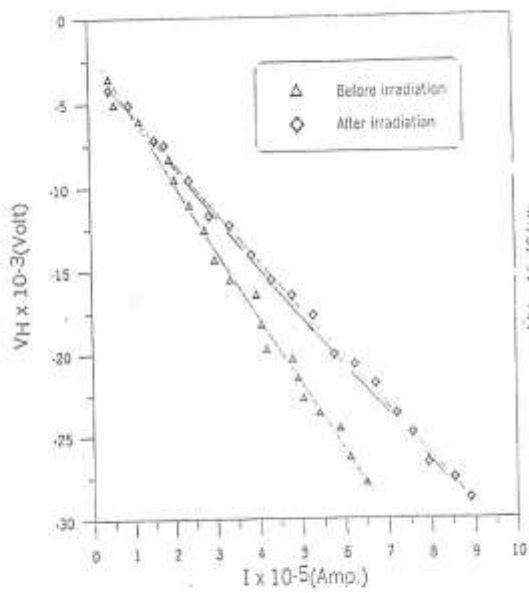


Fig.8

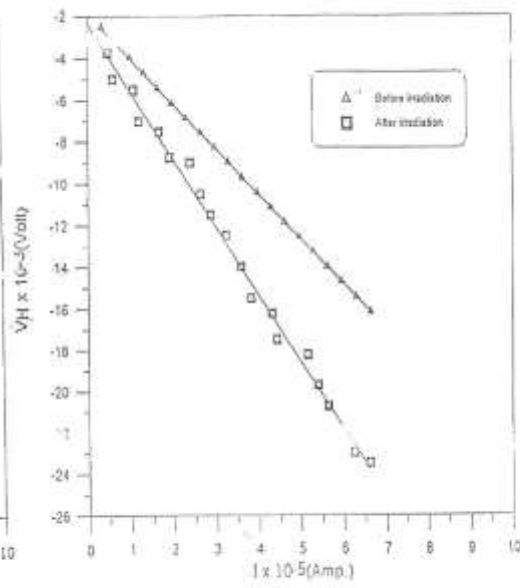


Fig.9

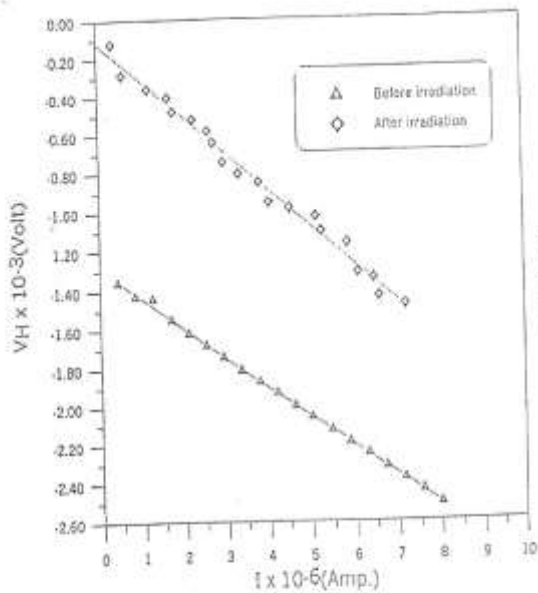


Fig.10

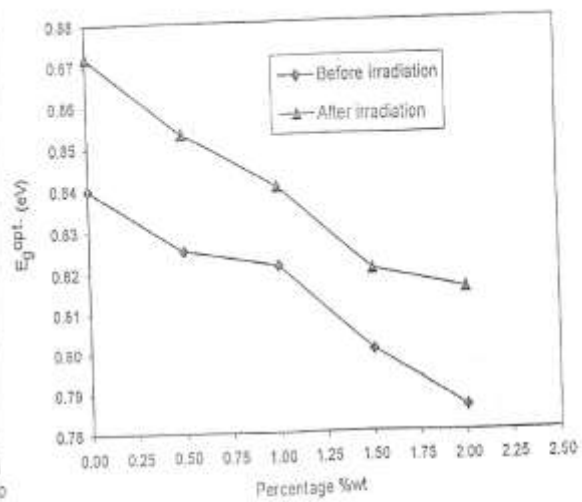


Fig.11