Iraqi Journal of Physics, 2010 *Vol. 8, No.12, PP. 18 - 22*

The Effect of Germanium Content(x) on the Electrical Properties of ($Ge_x S_{1-x}$) Thin Films

Bushra A. Hasan
Department of Physics, College of Science, University of Baghdad

Abstract

Thin films of Ge_xS_{1-x} were fabricated by thermal evaporating under vacuum of 10^{-5}Toor on glass substrate. The effect of increasing of germanium content (x) in sulfide films on the electrical properties like d.c conductivity (σ_{DC}), concentration of charge carriers (n_H) and the activation energy (E_a) and Hall effect were investigated. The measurements show that (E_a) increases with the increasing of germanium content from 0.1to0.2 while it get to reduces with further addition, while charge carrier density (n_H) is found to decrease and increase respectively with germanium content. The results were explained in terms of creating and eliminating of states in the band gap.

Keywords
Thin Film
Electrical Properties
$Ge_x S_{1-x}$

Article info
Received: Mar. 2010
Accepted: Apr. 2010
Published: Nov. 2010

تأثير تركيز الجرمانيوم على الخصائص الكهربائية لأغشية (Ge_xS_{1-x}) الرقيقة

بشرى عباس حسن
قسم الفيزياء – كلية العلوم – جامعة بغداد – الجادرية – بغداد - العراق

الخلاصة

تم تحضير أغشية رقيقة من $Ge_x S_{1-x}$ بطريقة التبخير الحراري تحت الفراغ 10^{-5} Toor على أرضية زجاجية. تم مناقشة تأثير المحتوى من الجرمانيوم على كل الخواص الكهربائية التي تشمل قياسات التوصيلية الكهربائية المستمرة، كثافة حاملات الشحنة وطاقة التنشيط وتأثير هول .أظهرت النتائج ان (E_a) تزداد مع زيادة محتوى الجرما نيوم من 0.1 الى 0.2 بينما تقل مع استمرار الأضافة .بينما وجدان كثافة حامالت الشحنة تقل ثم تزداد على التوالي مع زيادة المحتوى. فسرت النتائج بدلالة استحداث او ازالة مستويات في فجوة الطاقة.

Introduction

Amorphous chalcogenide semiconductors possess a lot of interesting phenomena, which reveal possibilities for using them in microelectronics and optoelectronics - as ovonic threshold and memory switching devices, inorganic photoresists, optical memory disks, etc. The increased interest in them has been connected mainly with their unique peculiarity to record information by irreversible or reversible structural transformations between a disordered and a more ordered state. Exposure to band gap light causes photoinduced changes, which have been studied in detail by K. Tanaka [1,2]. Especially, amorphous Ge-S thin films exhibit remarkable irreversible photo- and thermo-bleaching effects, caused by illumination and annealing, respectively [2,3]. GeS_2-based chalcogenide glasses containing other elements like Ga and La have been shown to provide satisfactory optical and thermal properties [4]

High purity germanium monosulfide was prepared by Chen et al [5] and its semiconducting properties were measured. Samples are obtained by the reaction of germanium and sulfur in vacuum at high temperature and reducing in ammonium gas to remove germanium disulfide. Dark resistivities of evaporated layers and polycrystalline blocks of GeS prepared by the above method are $10^{10}\Omega$ cm or more. The thermal activation energy for dark current is 0.74-t1.0eV and about 0.25-0.5eV at higher and lower temperature regions, respectively. The sign of the observed thermoelectric power is that of p type at high temperature, and its magnitude is about 1 mV/deg.

Experimental Part

In the present work, alloys of Ge_xS_{1-x} has been synthesized using high purity elemental germanium and sulfide is about (99.9999%) with different x content where (x = 0.1, 0.2 and 0.3). Stoichiometric amounts of the elements are placed in a quartz ampoule, The quartz ampoule was cleaned carefully with water and alcohol, respectively to remove dust, grease, and other possible contaminants, which is evacuated to a vacuum of 10^{-2} Torr and then sealed. The sealed ampoule is placed in a furnace, and then heated at a rate of $60C^0$ per hour in steps up to 1000 K. The ampoule is maintained at this temperature for about five hours and then allowed to cool slowly to room temperature. Thin films of Ge_xS_{1-x} with (x = 0.1,0.2 and 0.3) of $\approx$150nm thickness were prepared using thermal evaporation on corning glass slides substrates which were used which were subjected to several cleaning stages, and the distance of the source to substrate was 15cm. The evaporation carried out using Edward coating unit (model E306A) that was evacuated by means of oil-diffusion and rotary pumps. During the evaporation of the films, the pressure in the system was 4×10^{-5} Torr. All the samples were prepared under constant condition:- pressure, , substrate temperature (room temperature) and thickness. After the deposition process was ended the current supply was switched off and the samples were lifted in high vacuum for several hours, then the air admitted to the chamber, and the films were taken out from the coating unit and the measurements were made.

Finally, all the prepared films thermally treatment under vacuum of 10^{-2}Torr at different temperature (373 and 423K) for one hour then the measurements was made.

The structures of the prepared alloys and thin films are demonstrated by X-ray diffraction at room temperature (Siemens D500 diffract meter; CuKα1 radiation, λ = 1.5405 ˚A) of the samples).The diffraction patterns, In contrast, for Ge_xS_{1-x} alloys the can be indexed according to American Slandered for Testing (ASTM)cards as polycrystalline structure with hexagonal unit cell .X-ray diffraction of $Ge_x S_{1-x}$ alloys for (x=0.1,0.2and0.3) declared sharp diffraction peaks located at23^0 ,26^0 ,28^0,35^0,and 57^0, and the addition of Ge increases the polycrystalline degree which is obvious from the increasing of peak heights in the diffraction pattern of the alloy for x=0.3,also the increasing of Ge is responsible about the disappearing of the peak at $2\theta=36^0$,in contrast the total absence of Bragg peaks is clearly evident that Ge_xS_{1-x}thin films , justifies the classification of these samples as amorphous..

For intrinsic semiconductors the electrical conductivity is the sum of the two conductivities for electrons σ_n and holes σ_p, then the electric conductivity in an intrinsic semiconductors is.

$$\sigma_i = \sigma_n + \sigma_p \ldots\ldots\ldots\ldots\ldots(1)$$

where μ_n and μ_p are the electron and hole motilities respectively.

For intrinsic semiconductors n = p = n_i where n and p are the concentrations of electrons and holes and are measured in units of (cm^{-3}) , one can gets.

$$\sigma_i = n_i q(\mu_n + \mu_p)\ldots\ldots\ldots\ldots (2)$$

Where μ_n and μ_p are the mobility of electrons and holes respectively in units of (cm^2/V.sec). e is the charge of electron .The change of electrical conductivity with temperature of semiconductors are given by the equation [5]:-

$$\sigma = \sigma_0 e^{(-\frac{E_a}{k_B T})} \ldots\ldots\ldots\ldots\ldots (3)$$

Where E_a is the thermal activation energy ,T is the absolute temperature ,k_B is the Boltzmann constant and σ_0 is the minimum metallic conductivity (the value of σ when $T \rightarrow \infty$) Hall effect results from applying magnetic field (B_z) along a rectangular sample normal to the direction of current (I),the charge carriers will tend to be deflected to one side ,then building up potential gradient perpendicular to magnetic field and current ,this effect was used to determine the type and the density of charge carriers(n_H).Hall coefficient (R_H) is given by:

$$R_H = \frac{V_H}{I}\frac{t}{B_z} \ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Where t is the film thickness, the density of charge carriers is given by the relation:-

$$R_H = -\frac{1}{n_H e} \ldots\ldots\ldots\ldots\ldots.. \text{(5)}$$

The mobility of Hall (μ_H) is given by the relation [5] :-

$$\mu_H = \sigma\left|R_H\right| \ldots\ldots\ldots\ldots\ldots .\text{(6)}$$

Vacuum evaporated aluminum electrodes at the bottom of substrates were Previously done for electrical properties measurements.D.C electrical conductivity measurements were carried out at the temperature range (303-500) K using the electrical circuit which is consists of Oven type Herease ,Power supply and Ameter .The resistivity (ρ) of Ge $_xS_{1-x}$ samples deposited at room temperature were obtained using the following equation :-

$$\rho = \frac{Rwt}{L} \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad \text{(7)}$$

Where L and w are the length and the width of sample respectively and R and t are the resistivity and thickness of the film, the conductivity of the mentioned samples were obtained from the relation:-

$$\sigma = \frac{1}{\rho} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad \text{(8)}$$

The measurements of the charge carrier density and Hall mobility were provided from applying equations (5and6) respectively.

Results and Discussion

If there exists a large band gap amorphous material, it results in low electrical conductivity. But, these materials can be chemically modified and by controlling the states in the gap, the conductivity changes over many orders of magnitude can be controlled.

The electrical conductivity and activation energy of the Ge $_xS_{1-x}$thin films with different Ge content had been measured for as deposited and annealed at temperature (373,423) K. Plots of Lnσ versus 1000/T were the Ge content changes from (x=0.1-0.3) wt. % with different annealing temperature are shown in Figs. (1to3). One can distinguish two different regions in the temperature range, one such region is at low temperatures from 293.25to423.9Kand the other region is in high temperature range from 432.9to492.6)K. From measurements the values of electrical conductivity ($\sigma_{d.c}$) and activation energies (E_{a1},E_{a2}) were calculated and displayed in Table (1).

As shown from the results for Ge $_xS_{1-x}$ thin films the conductivity ($\sigma_{d.c}$) decreases with increasing of annealing temperature two and one order of magnitude for x=0.1 and 0.2 respectively , indeed ($\sigma_{d.c}$) decreases from $3.236\text{x}10^{-5}$ to $8.985\text{x}10^{-7}$ and from $9.611\text{x}10^{-5}$ to $6.166\text{x}10^{-6}$ $(\text{ohm.cm})^{-1}$ with the increasing of thermal treatment temperature from 303 to 423K,While ($\sigma_{d.c}$) exhibit to change in opposite manner for Ge $_{0.3}S_{0.7}$,i.e. ($\sigma_{d.c}$)increases $2.408\text{x}10^{-5}$ to $9.423\text{x}10^{-5}$ $(\text{ohm.cm})^{-1}$ with the increasing of annealing temperature.

Our data declare the inverse relation between the activation energies values and ($\sigma_{d.c}$) values i.e. ($\sigma_{d.c}$) increases when germanium content increase from 0.1to 0.2 , while it get to decrease for the residual value of x , this can be explained as follows:

The addition of Ge to S increases the electrical conductivity of S at the first time since Ge introduces new states in the band gap, the continues addition of Ge to S will compensates the vacancy and other states which will increase the resistivity or inhibits the high conductivity of the samples.

The main features characterizes the structure of sulfur S atoms are tetrahedral voids the addition of germanium to it make the Ge atoms distributed in an ordered manner over these voids in the first stage ,while the continues addition of Ge to S will creates new stats in the band gap of sulfide. An extended calculation of the electronic structure, and electrical resistivity measurements confirm the expected semiconducting behavior of Ge in S.

Table (1) illustrates the values of activation energies E_{a2} and E_{a1} for as deposited Ge $_xS_{1-x}$ thin films and annealed at (T_a=373and 423) K .

The interesting result is the appearance of on conductivity stage for the high germanium content ,i.e. at x=0.3 annealed at 423K which accompanies the most high concentration of charge carriers. The formation of Ge-Ge bonds at high germanium content resulting in the increasing of hole concentration on the valance band.

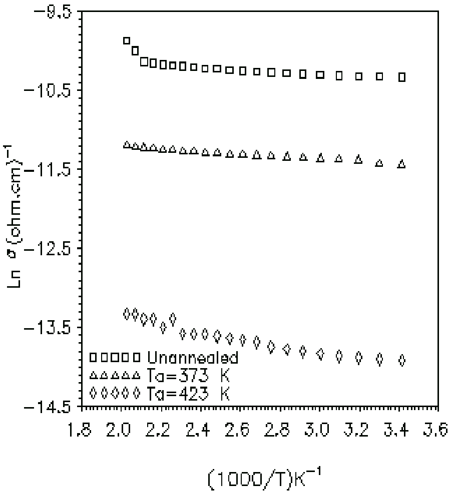

Fig.(1) :The variation (lnσ)versus(10^3/T) of as deposited Ge $_{0.1}S_{0.9}$ thin annealed at different temperatures.

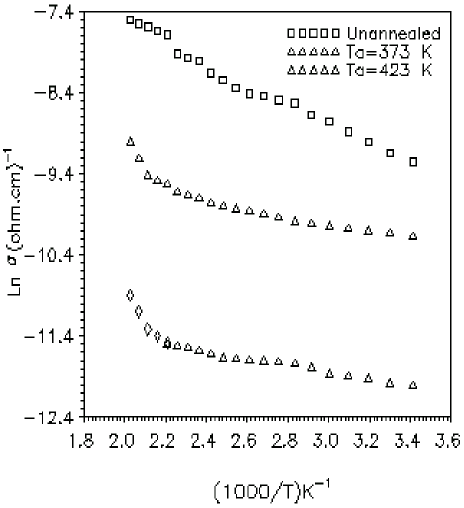

Fig.(2): The variation (lnσ)versus(10^3/T) of as deposited Ge $_{02}S_{0.8}$ thin annealed at different temperatures.

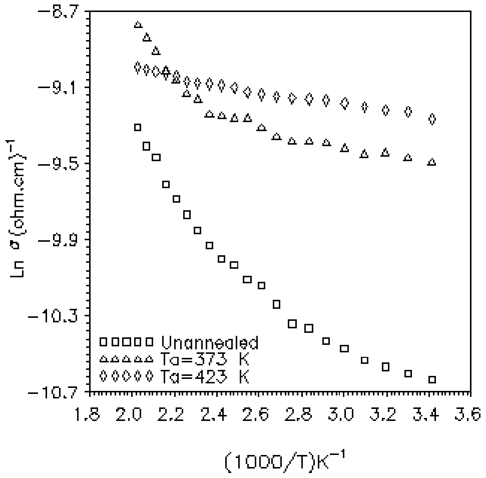

Fig.(3) The variation (lnσ)versus(10^3/T) of as deposited Ge $_{0.3}S_{0.7}$ thin annealed at different temperatures.

Table (1) the values of activation energy E_{a2} ,E_{a1}, conductivity ($\sigma_{d.c}$),The concentration of charge carriers n_H, and the type of conductance as function of annealing temperature of Ge $_xS_{1-x}$ thin films

Ge content (x)wt.%	Annealing Temp.(K)	($\sigma_{D.C}$) (Ω.cm)$^{-1}$ at R.T	(E_{a1}) (eV)	Temp. Range (K)	(E_{a2}) (eV)	Temp. Range (K)	n_H (cm^{-3})	Type of conductance
0.1	303	3.236×10^{-5}	0.0114	293.25-432.9	0.1450	432.9-492.6	2.53×10^{13}	n
	373	1.087×10^{-5}	0.0203	293.25-432.9	0.1540	432.9-492.6	1.636×10^{12}	n
	423	8.985×10^{-7}	0.0304	293.25-432.9	0.0641	432.9-492.6	2.335×10^{11}	n
0.2	303	3.236×10^{-5}	0.0114	293.25-432.9	0.1444	432.9-492.6	2.850×10^{13}	n
	373	1.087×10^{-5}	0.0203	293.25-432.9	0.2503	432.9-492.6	2.949×10^{13}	n
	423	8.985×10^{-7}	0.0304	293.25-432.9	0.2797	432.9-492.6	3.866×10^{13}	p
0.3	303	3.236×10^{-5}	0.0114	293.25-432.9	0.1892	432.9-492.6	2.53×10^{10}	P
	373	1.087×10^{-5}	0.0203	293.25-432.9	0.1194	432.9-492.6	1.6997×10^{11}	P
	423	8.985×10^{-7}	0.0304	293.25-492.6		432.9-492.6	1.5870×10^{16}	p

Our data for Hall effect measurements referred that Ge $_x$ S_{1-x} thin films in the hole composition (x=0.1-0.2) were n-type (R_H is negative),i.e. there is inverse relation between the current (I) and Hall voltage (V_H),thus the created electric field [inhibit the passage of the charge carriers (electrons) consequently the out put current will be decreased with increasing the applied electrical field converts to p-type (R_H is positive), i.e. there is direct relation between the current (I) and Hall voltage (V_H),thus the created electric field [permits the passage of the charge carriers (electrons) consequently the out put current will be increased with increasing the applied electrical field for the residual x value, our data show that the increase of Ge content in the prepared samples convert the conductance of form from n to p type as a result of dominating the properties of Ge,since it is well known that Ge exhibits p-type conductance. On the other hand our data reveal that the high conductivity (high charge density) always accompanies the p-type conductance while poor conductivity (lower charge density) accompanied n-type conductance.

Conclusion

According to the above observations, the following conclusion are drown :- (1) the addition of (Ge) to S regards as agent factor to introduces or compensates the states or vacancies in the band gap. (3) the addition of (Ge) to S make ($\sigma_{d.c}$) varies in non systematic manner.(4)The increases of (Ge) content in $Ge_x S_{1-X}$ films converts the type of conductance.

References

[1] K. Tanaka, Reviews of Solid State Science (World Scientific Publishing Company, 1990,p. 641.

[2] K. Tanaka, Y. Kasanuki, A. Odajima, Thin Solid Films, **117,** 251, 1984.

[3] T. Kawaguchi, S. Maruno, K. Masui, J. Non-Cryst. Solids, **97&98,** 1219 (1987).

[4] M.Bilkova ,O.Nemec,M.Frumar,j.Opto electron.Adv.Mater,7(5),2247, 2005.

[5] CHEN X. -A. (1); ONODA M. (1); WADA H.(1); SATO A. (1); NOZAKI H. (1); HERBST-IRMER R. (2); Journal of Solid State Chemistry **ISSN** 0022-4596, 1999, vol. 145, no.1, pp. 204-211.

[6] S. Sze, Physics of Semiconductors Devices, John Wiley and Sons, New York, 2007.