Glass-crystal transformation of amorphous Ge_xSb_{40-x} Se_{60} films

El-Sayed M. Farag[a] and Ahmed Abo-Arais[b]
[a]Basic Science of Eng. Dept., Faculty of Eng., Shebin El-Kom, Minufiya University, Menouf, Egypt
Email: awsymkh@yahoo.com
[b] Physics and Mathematics Eng. Dept., Faculty of Electronic Eng., Minufiya University, Menouf, Egypt
Email: Ahmedabo70@yahoo.com

Chalcogenide glasses of Ge_xSb_{40-x} Se_{60}, where x = 10, 20, 30 and 40 at. % were prepared from elements in sealed evacuated silica ampoules ≈ 10^{-4} Torr. Amorphous films have been prepared by thermal evaporation technique. To study the glass-crystal transformation for Ge-Sb-Se glassy system, the films were annealed at 490 K for 2h, and investigated by X-ray diffraction patterns. The results showed a crystallization of the annealed films with different degrees depending on the excess of the coordination number due to Ge substitution of Sb atoms. Electrical conductivity measurement has been carried out on as-deposited and annealed films in the temperature range 300-500K. The results indicated that the conductivity of the annealed films is higher than as-deposited films which confirmes the transformation of the amorphous films to a crystalline state as derived from X-ray diffraction analysis. The obtained results are explained according to the presence of nucleation centers for crystallization due to Ge substitution of Sb atoms which grows by annealing.

تم تحضير عينات زجاجيه من المركب Ge_xSb_{40-x} Se_{60} حيث(x=10,20,30,40) فى امبولات من السليكا المفرغة ثم تم تحضير الأفلام الرقيقه بواسطة تقنية التبخير الحرارى. لدراسة التحول من التركيب الزجاجى إلى اتركيب البللورى للافلام المحضرة تم احماء الأفلام عند درجة حرارة (490K) لمدة ساعتين وفحصها بالأشعه السينيه التى اظهرت تبلر الأفلام بدرجات متفاوته معتمدة على الزياده فى عدد المجاوره تبعا لاحلال الجرمانيوم مكان الأنتيمون. تم قياس معامل التوصيل الكهربى فى مدى حرارى (300-500K) للافلام المحضره وكذلك للافلام التى تم احماؤها عند (490K) لمدة ساعتين. لوحظ تحول ميكانيكية التوصيل من خاصية توصيل القفز الى خاصية توصيل شبه الموصلات الذاتى بقيم مختلفة لطاقات التنشيط. وقد تم تفسير التغير فى طاقة التنشيط ومعامل التوصيل الكهربى نتيجه لتبلر الأفلام المحماة. أظهرت النتائج ان التوصيل الكهربى للعينات المحماة أعلى من العينات المحضرة وهذا يؤكد التحول من التركيب العشوائى إلى التركيب البللورى الذى اظهرته تحليل الأشعه السينيه. تم تفسير النتائج تبعا لوجود أنويه للتبلر بإضافة عنصر الجرمانيوم الرباعى بدلا من عنصر الانتيمون الثلاثى التكافؤ وتنمو أنوية التبلر بواسطة عملية الأحماء الحرارى للعينات.

Keywords: Amorphous, Ge,Sb,Se, Films, Crystal, Conductivity

1. Introduction

Studies of chalcogenide films are of interest because of their unique electrical and optical properties [1]. Chalcogenide glasses have received much attention due to their potential use in various solid state devices. The nature of the gap states in these semiconductors is fundamental for a better understanding of their electrical and optical properties.

Recently, investigations of Ge-Sb-Se glasses are mainly concerned with the glass forming region and electrophysical properties as a function of compositions [2-4]. Characterization of the optical and electrical properties in these glasses has been extensive [5-8]. The suitability of these glasses for an application often depends upon their mechanical properties [9]. Amorphous chalcogenide films show widely differing conductivity data depending on the preparation techniques [10]. Controlled crystallization of glass, leads to the separation of a crystalline phase from the glassy parent phase in the form of tiny crystals where the number of crystals, growth rate and crystal size are controlled by suitable heat-treatment [11].

The dependence of the electrical properties of Ge-Sb-Se glasses on their chemical composition are also of interest, especially in considering the effects of the average coordination number, *z*, of covalent bonds per atom. This number is a measure representing

structures of atomic units [12]. Upon examing the amorphous structure of covalent glasses, we may classify building elements into two components [13], one is normal bonding structure consisting of covalent bonds of densities of the order of 10^{22} –10^{23} cm^{-3}, which can be specified by chemical and topological natures, and the other is defects, e.g., impurities, dangling bonds, valence-alternation pairs, and wrong bonds (homopolar bonds in stoichiometric alloys). The density of defective bonds is, in general, less than 10^{-2} of that for the covalent bonds, and therefore, structural behaviors are determined mostly by the normal configurations.

In the present work an attempt is made to detect whether any unusual compositional dependence of electrical parameters exists in $Ge_xSb_{40-x}Se_{60}$ films, such as the conductivity and the activation energy. The electrical properties are measured in the temperature range 300-500 K. Also, we investigate the electrical conductivity and structural properties after annealing at 490 K for 2h.

2. Experimental procedure

$Ge_xSb_{40-x}Se_{60}$ glasses with x = 10, 20, 30, and 40 at.% were prepared from elements of 99.999 % purity. Appropriate quantities from the elements were sealed into silica ampoules after evacuation to a pressure of 10^{-4} Torr. They were heated to 1300 K in a furnace and after homogenization for 10h, the liquids were quenched in ice coled water.

Thin films have been prepared by thermal evaporation techniques (Edward 306 E, using molybdenum boat) under a vacuum of 2×10^{-5} Torr. Thin films were deposited on clean glass substrates at room temperature (300 K). The film thickness was 300 nm determined by quartz crystal thickness monitor (FTM5) and also interferometically. The films structure was amorphous as checked by X-ray diffraction as shown in fig. 1.

Electrical conductivity was recorded for amorphous films and after annealing at 490 K as a function of temperature in the temperature range 300-500 K. To measure the resistance, silver paste was used to attach the terminals. The structure of the films was checked by X-ray diffraction after annealing and analysed.

3. Results and discussion

3.1. Crystallization products

X-ray diffraction results show that the as-deposited samples have amorphous structure. But the samples annealed at 490 K for 2h were crystalline. The annealing temperature was selected to be between the glass transition temperature, T_g, and the crystallization temperature, T_c, as produced by the DT analysis traces. The X-ray diffraction technique is used to determine the phases present and the orientation of polycrystaline $Ge_xSb_{40-x}Se_{60}$ films deposited by thermal evaporation. X-ray diffraction pattern was recorded within the diffraction angle range 10-60° as shown in fig. 1. The peaks were selected to investigate the crystalline phases and the crystalline structure of each phase. Table 1 illustrates the X-ray analysis of the obtained peaks. The main crystalline phases were $GeSe_2$ and Sb_2Se_3 as matched by ASTM cards. In addition to this, an unknown two phases at composition $Ge_{10}Sb_{30}Se_{60}$ were detected by the peaks *f* and *g* which were located around the diffraction angle 48.5°. There is no ASTM cards for it and it may be suggested to be a GeSbSe crystalline phases [3]. While at composition $Ge_{30}Sb_{10}Se_{60}$ the unknown phase was detected by the peak (*f*), which was located around the diffraction angle of 48.2°. There is no ASTM cards for it and also it may be suggested to be a GeSbSe crystalline phase. The intensity of the peaks *b* and *d* decreases with decreasing Sb content or increasing Ge content as shown in fig. 1. In a random-network model of GeSbSe glasses, the preservation of nearly optimal bond lengths cause fluctuation in bond angles and Van der Waals distances. These local fluctuations may be large enough to give rise to electronic or vibrational properties quiet different from those of the typical bonding configurations in the random-network model. Such fluctuations, then contribute to tails of localized states on the valence and conduction bands [14].

The average coordination number, *z*, is a molar average and is given for Ge_x Sb_{40-x} Se_{60} films by [15]:

$$Z = [4x + 3(40-x) + 2 \times 60]/100. \quad (1)$$

Table 1
X-ray crystallographic data of a-$Ge_xSb_{40-x}Se_{60}$ films after annealing at 490k for 2h

Experimental					ASTM cards		
Composition x at.%		2θ	d(nm)	Crystal phase	d(nm)	(hkl)	Crystal form
10	a	----	---	---	---	---	---
	b	23.7	0.316	$GeSe_2$	0.316	(123)	Monoclinic
	c	28.7	0.382	Se	0.386	(-202)	---
	d	40.2	0.529	Sb_2Se_3	0.525	(120)	Orthorhombic
	e	47.3	0.617	$GeSe_2$	0.615	(020)	---
	f	48.5	0.632	---	---	---	---
20	a	---	---	----	---	---	---
	b	23.7	0.316	$GeSe_2$	0.316	(123)	Monoclnic
	c	27.7	0.369	$GeSe_2$	0.367	(115)	------
	d	40.0	0.527	Sb_2Se_3	0.526	(201)	Orthorhombic
30	a	18.7	0.250	Sb_2Se_3	0.251	(231)	Orthorhombic
	b	23.7	0.316	Sb_2Se_3	0.316	(112)	Orthorhombic
	c	26.3	0.350	$GeSe_2$	0.350	(132)	Monoclinic
	d	40.2	0.529	Sb_2Se_3	0.526	(201)	Orthorhombic
	e	47.0	0.614	$GeSe_2$	0.615	(020)	---
	f	48.2	0.629	---	---	---	---
40	a	18.7	0.25	$GeSe_2$	0.251	(223)	Monoclinic
	b	23.7	0.316	Se	0.320	(400)	---
	c	25.0	0.333	$GeSe_2$	0.335	(113)	Monoclinic
	d	40.2	0.529	Sb_2Se_3	0.526	(201)	Orthorhomic

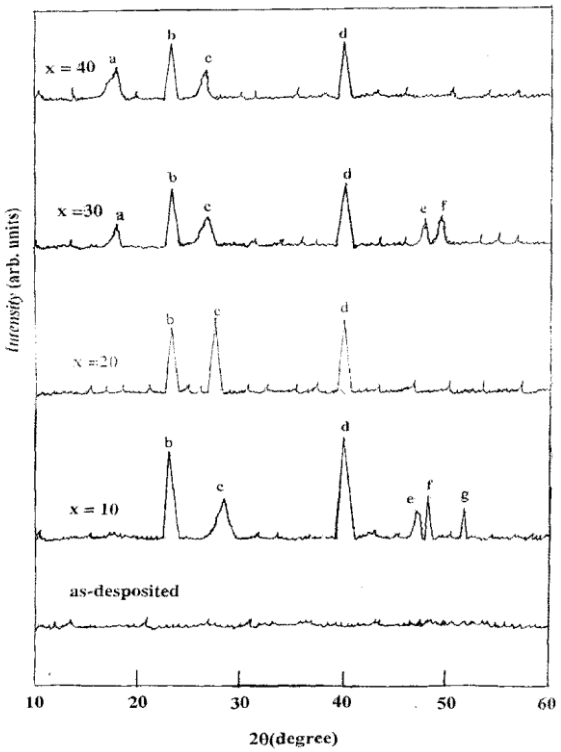


Fig.1. X-ray diffraction of a-$Ge_xSb_{40-x}Se_{60}$ films as-deposited and annealed at 490 K for 2h.

The rule suggests that the numbers of nearest-neighbor atoms for Ge, Sb and Se are 4,3 and 2 respectively. A 2-dimensional drawing of the structure of lightly cross-linked Ge-Sb-Se films is given [9]. The presence of the cross-linking atoms turns the structure of the glass from 1- dimensional Se chains into a 2-dimensional or 3-dimensional structure depending upon the degree of cross-linking [16-17]. Each composition belongs to the pseudobinary line $(Ge_2Se_3)_x$ $(Sb_2Se_3)_{1-x}$ for the nonstoichiometric Ge_2Se_3 [12]. These glasses may be considered chalcogenide deficient and therefore, Se-Se bonds by analogy with $(Ge_2S_3)_x$ $(Sb_2S_3)_{1-x}$ system can be assumed to be absent [18]. Satisfying coordination numbers of individual elements Ge-Se, Sb-Se, Ge-Sb, Ge-Ge and Sb-Sb bonds can be expected.

3.2. Electrical conductivity

The d.c. conductivity was measured as a function of temperature in the range 300-500 K. Heating was done at the rate of 3 to 5 K/min. The d.c. conductivity dependence on temperature before and after annealing fits well to the relation

$$\sigma = \sigma_o \, exp\,(-E_a/kT). \qquad (2)$$

where σ_o is the pre-exponential factor (Ω^{-1} cm^{-1}), E_a is the activation energy (eV) and k is the Boltzman constant. The virgin films were pretreated by heating to 500 K and cooling back to 300 K in air. This step was repeated before starting film characterization in order to clean the samples of defects [19]. Therefore, the conductivity during the cooling cycle closely coincides with that in the heating cycle in vacuum ≈ 10^{-2} Torr. Hence, for all our calculations, we have used the data of the films during the heating cycle. It can be seen that the conductivity increases with increasing temperature but that increase is slow in the low temperature region. Fig. 2 shows that as the temperature increases, the samples transform from hopping conducting to intrinsic semiconductor. Accordingly, the activation energy of conduction has been changed from narrow hopping gap (E_h) to wide activation energy (E_a). This dependence shows a sharp increase of the conductivity at a certain temperature T_{kink}. Two straight lines were obtained confirming the semiconducting behavior as shown in fig. 2. The position of T_{kink} dependence of Ge content, it shifts to higher temperature with decreasing Ge content or increasing Sb content. Fig. 3 shows the calculated energies for each region against the atomic percent of Ge. The hopping energy, E_h, decreases with increasing Ge content or decreasing Sb content in the $Ge_xSb_{40-x}Se_{60}$ system. The presence of a hopping regime strongly suggests important localized states as band tails, that may decrease with decreasing Sb content or increasing Ge content, while, the wide activation energy, E_a, increases withincreasing Ge content. According to pauling [20] the single bond energy of the Ge-Se bond is larger than that of the other bonds present in the system. Therefore, for the Ge-rich compositions, the activation energy, E_a, would be larger than that for the Sb-rich films. Also, for the Ge-rich films, it is assumed that excess Ge atoms form bonds amongst themselves after the Ge-Se and Sb-Se bonds are all formed. As Ge-Se bonds are stronger than Sb-Se bonds, it is very likely that more than the expected number of Ge-Se bonds are formed in the place of some of the Sb-Se bonds [21].

Annealing of the films at 490 K for 2h, has pronounced effect on the crystallinity of the film as should be evident from X-ray diffraction patterns shown in fig. 1. The variation of d.c. conductivity with temperature of the $Ge_xSb4_{0-x}Se_{60}$ system after annealing is shown in fig. 4. It is seen that the variation of ln σ with 1/T is linear for all compositions, indicating thereby that each composition has a single activation energy for the conductivity. We can observe the change of the value of both activation energy, E_a(eV), and conductivity due to crystallization deduced from our X-ray diffraction patterns. Therefore, the activation energy of the annealed films is lower than that of the as-deposited films as shown in fig. 5-a. The activation energies for as-deposited films and annealed films as a function of average coordination number, z, are given in fig. 5-b. The results show that the activation energy increases almost linearly with increasing the average coordination number. In $Ge_xSb_{40-x}Se_{60}$ films, with

increasing average coordination number, the number of chalcogenide atoms remains constant but the number of Ge-Se bonds increases and the average bond energy of the Ge-Sb-Se system increases as well [12].

4. Conclusions

We present here electrical conductivity measurements on $Ge_xSb_{40-x}Se_{60}$ films prepared by evaporation. The as-deposited films were amorphous, and were annealed at 490 K for 2h. Thermal crystallization and X-ray structure analysis of devitrified materials have been carried out on Ge-Sb-Se films. These investigations show the following notable features:

1. The results show that the conductivity of annealed films is higher than that of as-deposited films, due to transformation of the amorphous films to the crystalline state.
2. The structural analysis revealed that the formation and the properties of as-deposited amorphous Ge_xSb_{40-x} se_{60} films are very sensitive to annealing temperature. The annealed $Ge_xSb_{40-x}Se_{60}$ films undergo a structural change from glassy to crystalline forms, which can be related to a phase transition, where the predominantly two-dimensional layer-like structure changes to a three-dimensional network.
3. The glass-crystal transformation of the amorphous Ge-Sb-Se system opens the pathway towards new devices.

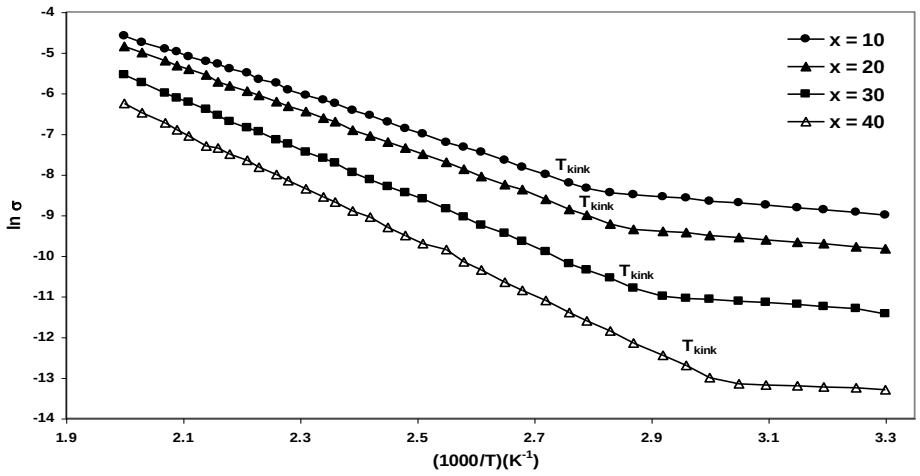


Fig. 2. Variation of ln σ with 1000/T for amorphous $Ge_xSb_{40-x}Se_{60}$ films.

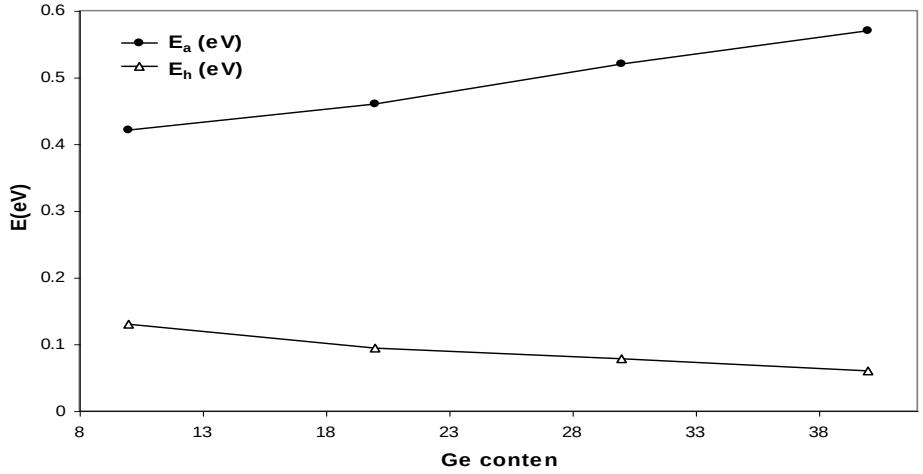


Fig. 3. Variations of hopping and activation energy with Ge content for a-Ge_xSb_{40-x} Se_{60} films.

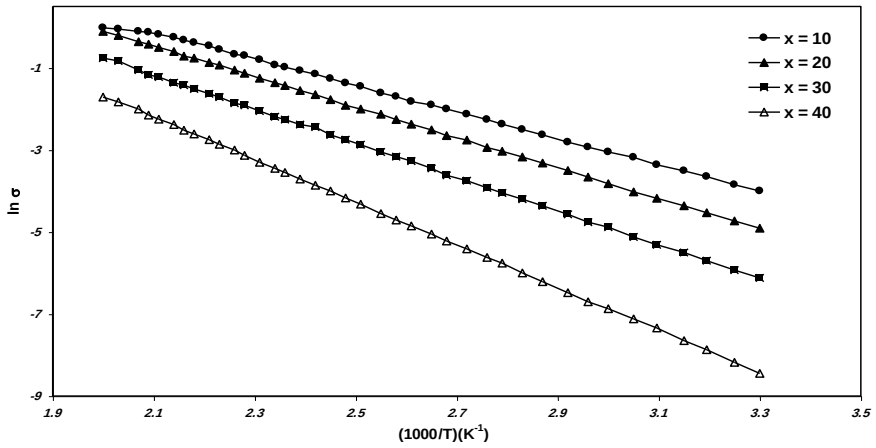
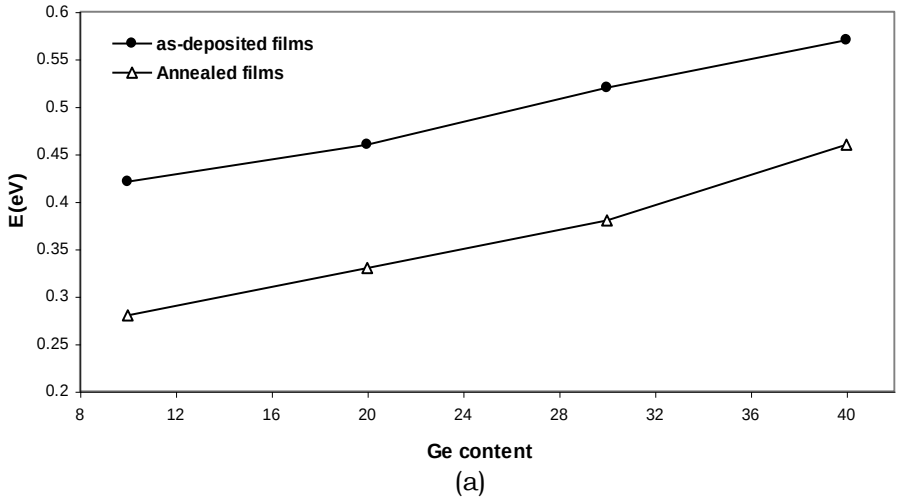
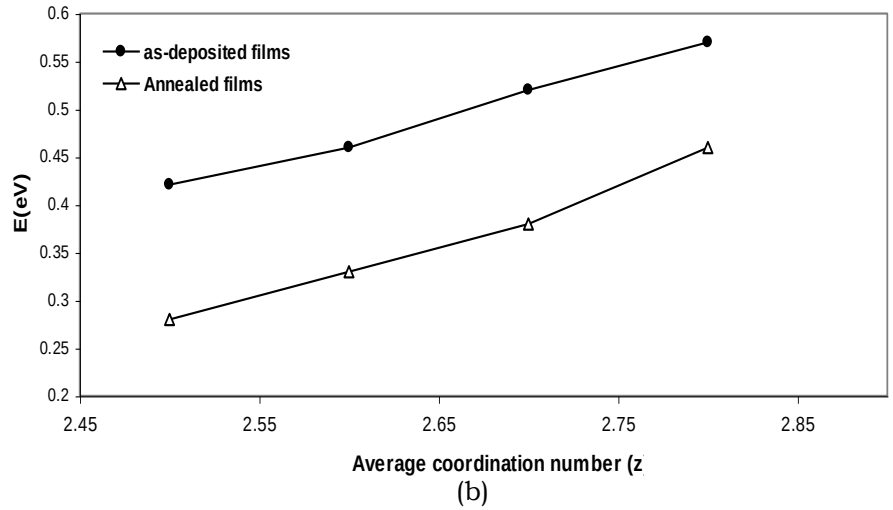


Fig. 4. Variation of ln σ with 1000/T for amorphous $Ge_xSb_{40-x}Se_{60}$ films after annealing at 490 K for 2h.



(a)



(b)

Fig. 5-a. Variation of activation energy as-deposited and annealed films with Ge content for a-$Ge_xSb_{40-x}Se_{60}$ films.
(b) Variation of activation energy as-deposited and annealed films with average coordination number, z, for a-$Ge_xSb_{40-x}Se_{60}$ films.

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