Structural , Morphological and Electrical Properties of $AgSbSe_2$ Thin Films

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Abstract

$AgSbSe_2$thin films with different thicknesses (100,300,500, and 700nm) have been deposited by single source vacuum thermal evaporation onto glass substrates at ambient temperature to study the effect of thickness on its structural morphology, and electrical properties. The X–ray diffraction patterns of $AgSbSe_2$thin film show that with low thickness (t=100,300 and 500nm) have amorphous structure convert to polycrystalline structure with increase thickness to 700 nm..AFM measurements show that the average grain size increases while the average surface roughness decreases with the increase of thickness. The DC conductivity of the vacuum evaporated $AgSbSe_2$thin films was measured in the temperature range (298-473)K and was found to increase on order of magnitude with increase of thickness. The plot of conductivity with reciprocal temperature suggests, there are two activation energies Ea_1, andEa_2 for $AgSbSe_2$for all and thicknesses which decrease with increasing thickness. The electric carrier concentration and mobility show opposite dependence upon thickness.

Keywords: $AgSbSe_2$thin films, D.C,XRD.

الخواص التركيبية والكهربائية لاغشية AgSbSe2 الرقيقة

الخلاصة

تم تحضير اغشية رقيقة من $AgSbSe_2$ باسماك مختلفة (t=100,300 , 500and 700nm) عند درجة حرارة الغرفة على قواعد من الزجاج استخدام طريقة التبخير الحراري وتحت الفراغ لدراسة تأثير السمك على الخواص التركيبية والكهربائية. طيف الاشعة السينية اظهر ان اغشية $AgSbSe_2$ وعند الاسماك الواطئة t=100,300 , 500 كانت لها ذات عشوائية التركيب تحولت الى متعددة البلورات عند زيادة السمك الى t=700nm. فحص مطياف القوى الذري اظهر ان معدل حجم الحبيبة لاغشية $AgSbSe_2$ ازداد بينما هبط معدل الخشونة مع زيادة السمك. قياس التوصيلية الكهربائية المستمرةلاغشية $AgSbSe_2$ المحضرة بالتبخير الحراري ضمن مدى درجات الحرارة(298-473)K اظهرت ان التوصيلية ازدادت رتبة واحدة مع زيادة السمك.العلاقة بين مقلوب درجة الحرارة ولوغارتم التوصيلية بينت ان هناك طاقتي تنشيط Ea_1 و Ea_2 لاغشية $AgSbSe_2$ لجميع الاسماك والتي تناقصت قيمهما مع زيادة السمك . كثافة حاملات الشحنة والتحركية ظهرت سلوكا معكوسا مع زيادة السمك.

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INTRODUCTION

The ternary chalcogenides $AgSbSe_2$ and $AgSbTe_2$ belongs to family of semiconductors with disordered NaCl cubic structure (s.g. Fm3m) in which silver and antimony occupy metal sublattice [1-3]. Alloys of both compounds either in single-crystal form or in thin-film form have received considerable interest owing to their optical and electronic properties. They are attractive phase-change (PC) materials used as a switching medium in rewritable optical memories [4-11].

The compound thin film exists in two phases-cubic $AgSbSe_2$ and orthorhombic Ag_5SbSe_4. Different techniques for the preparation of cubic $AgSbSe_2$ have been illustrated in the literature including, by fusing the constituent elements in a vacuum sealed quartz tube[12] •, vacuum evaporation[12-1413-15]and chemical deposition[15].Abdelghany *et al*.[16] • carried out measurements on the electrical conductivity and thermoelectric power of the $AgSbSe_2$ in the solid and liquid states from 350 to 975 ^oC. Wojciechowski *et al.*[17] • pointed out the semiconducting with a narrow band or semimetallic properties of this material by studying the electrical conductivity and the See back coefficient (320 V/K at room temperature) is measured as a function of temperature in the range from 300–600 K. Schmidt *et al.*

[18] • estimated the value of Eg of this material is 0.09 eV, indicating that the semi metallic feature and alloying of $AgSbSe_2$ compounds exhibit an apparent semiconducting behavior. The $AgSbSe_2$ have been studied previously, however, the literature survey showed that the D.C conductivity studies on the semiconductor $AgSbSe_2$ were not reported. In this work, we report the deposition of $AgSbSe_2$ thin films without *in situ* annealing using a reactive evaporation technique[19] •. To evaluate the potentiality of this material for optoelectronic and thermoelectric applications, the structural, morphology and electrical in the temperature range(298-473K) to enlighten the electron transport behavior, are studied and presented.

Experimental details

The compounds of *$AgSbSe_2$* were prepared by quenching technique. The exact amount of high purity (99.999%) (Ag,Sb, and Se) elements accordance with their atomic percentages were weighed 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 which containing the elements were heated to 1073K for 20 hours then cooled to room temperature. The temperature of the furnace was raised at a rate of10^oC/min. During heating the ampoules are constantly rocked .This is done to obtain homogeneous compounds. *$AgSbSe_2$*thin films of different thickness (t= 100,300, 500 and 700) nm were prepared using thermal evaporation by continuously feeding the material with a powder to a heated molybdenum boat of melting point about 2895K at which temperature instantaneous evaporation of the material takes place.

Corning glass slides substrates were used, and the distance of the source to substrate was 15 cm. The evaporation carried out using Edward coating unit (model E306A). During the evaporation of the films, the pressure in the system was $4x10^{-5}$ Torr. All the samples were prepared under constant condition [pressure, rate of deposition (3nm/sec), substrate temperature (room temperature). To study the electrical properties for the films Ohmic contacts for the prepared films are produced by evaporating (Al) electrodes of 300 nm thickness, by means of thermal evaporation methods. Then the d.c conductivity (σ) has been studied using the electrical circuit which is consists of oven type Herease and keithley (616). The thickness of the prepared films has been determined using Fizeau fringes of equal thickness are obtained in an optical aperture. The film thickness (t) is given by:

$$t = \frac{\lambda}{2}\frac{\Delta x}{x} \qquad \ldots (1)$$

Where

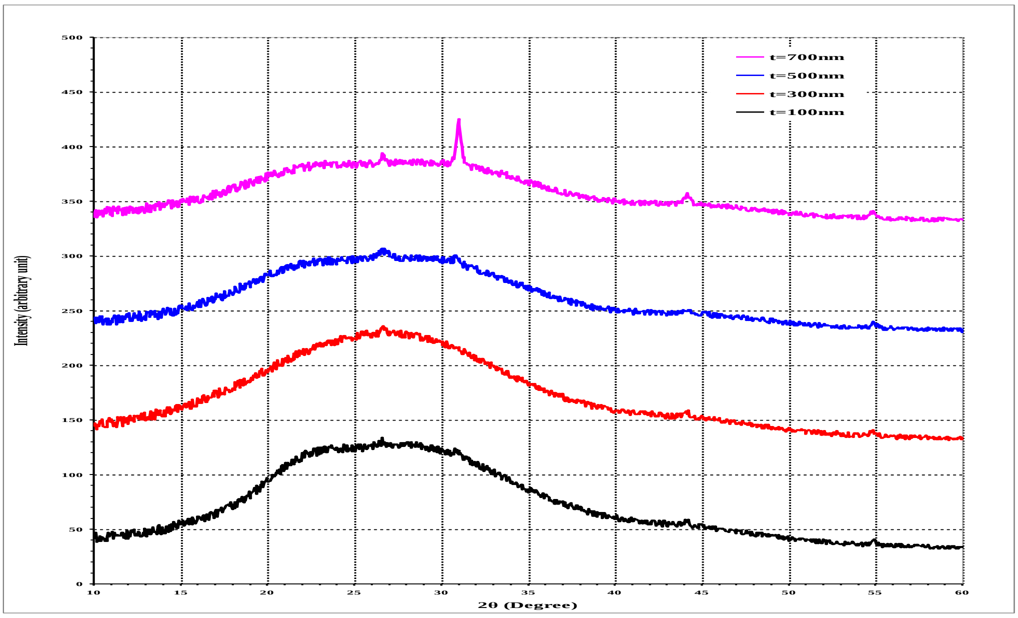
Δx is the shift between the interference fringes, x is the distance between the interference fringes and λ is the He: Ne wavelength (589.3 nm). The XRD measurements were done using diffractometer with Cu-Kα (λ= 1.5404 Å) radiation, operated at 30 kV, 20 mA**.** The average particle size (D) is calculated using the Scherrerformula as in Eq. (3). $D = \frac{0.9\lambda}{\beta\cos\theta}$ where λ is the wavelength of the X-ray used, β the full width at half maximum and θ the glancing angle.

Results and Discussion

The main purpose of this section is to investigate the structural type of semiconductor material that is relevant to the work and to ensure that the structure will not be changed after evaporation. Also, the effect of thickness on the films structure has been studied. The x-ray diffraction pattern of $AgSbSe_2$ thin films deposited at different thicknesses is shown in Fig.1. The thermally deposited $AgSbSe_2$thin films were found to be amorphous in the as-prepared form for low thickness(100, 300, and 500nm) . When thickness increase to 700nm, $AgSbSe_2$ thin films become polycrystalline , as found by XRD and Fig.1 The indexing of the pattern is done and the XRD data is compared with standard ASTM card and is shown in Table 1. The material was further characterized by structural and optical techniques. Small diffraction peaks appear located at 2θ=26.6°,31.01°,44.16° and 54.88° corresponding to diffraction planes (111),(200),(220)and(222).The well defined sharp peaks in the pattern suggest that the grains in the sample are randomly oriented along different crystallographic planes, which indicate the polycrystalline nature of the prepared sample. The structural analysis showed the filmsare single phase with a NaCl structure, which is in agreement with that reported by Wang *et al* [20]and Tipcompor et al [21] • . The prominent peak in the pattern corresponds to the reflection from the (200) plane. The relative intensities of the other peaks decrease since the penetration depth of the X-ray decreases as the angle increases.

Table(1) XRD parameter of as deposited $AgSbSe_2$ thin films with different thickness.

Thicnes s(nm)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Card No.
100	Amorphous						
300	Amorphous						
500	Amorphous						
700	26.620	0.3210	3.3459	25.4	(111)	3.3405	901-1029
	31.013	0.3060	2.8813	27.0	(200)	2.893	901-1030
	44.160	0.3854	2.0492	22.3	(220)	2.0457	901-1031
	54.880	0.3912	1.6716	22.9	(222)	1.6703	901-1032



Figure(1) XRD of as deposited $AgSbSe_2$ thin films with different thicknesses.

Fig.2 shows three dimensional AFM images of *$AgSbSe_2$*thin films grown having thickness100,300,500,700nm.Two-dimensional grain size of *$AgSbSe_2$*thin films were measured by using nano scale reading. It is obvious from table 2 that the average grain size get to increase with increase of thickness, indeed the grain size increases from 88 to 95 nm when the thickness increases from 100nm to 700nm . On the other hand the results showed that average roughness decreased with thickness, indeed the average roughness decreases from 1.04 to 0.855 when the thickness increases from 100 to 500nm , however the average roughness get to increase when the thickness increases to 700nm, the attributed to phase transformation from amorphous to polycrystalline structure.

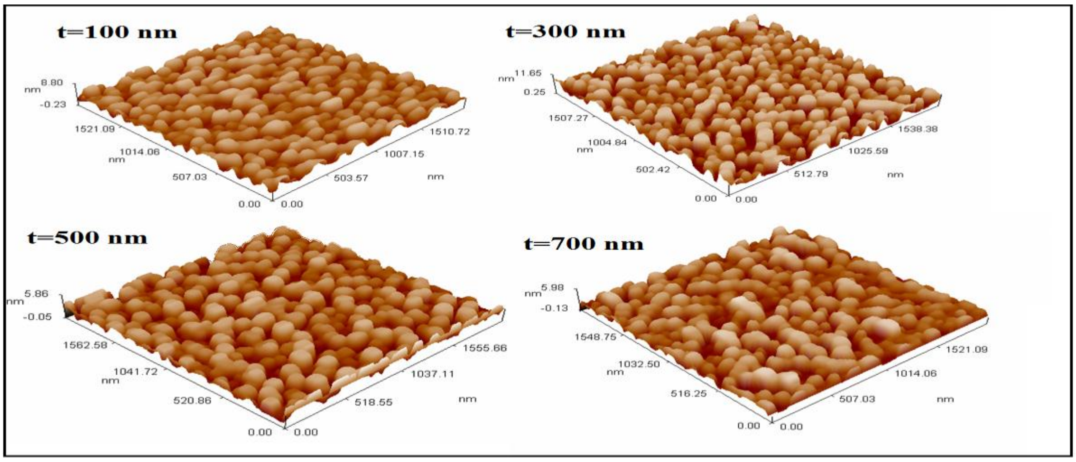


Figure (2) AFM images of $AgSbSe_2$ film deposited onto glass substrate with different thickness

Table (2) Average grain size and average roughness for $AgSbSe_2$ thin films with different thickness.

Thickness(nm)	Average roughness(nm)	Average grain size(nm)
100	1.04	88.15
300	1.89	79.27
500	0.855	94.98
700	0.883	95.83

Studies of temperature dependences of electrical conductivity revealed that $AgSbSe_2$ exhibit semiconductor behavior. For all the films, conductivity follows the relation

$$\sigma = \sigma_o \exp(-\frac{E_a}{k_B T}) \qquad \ldots(2)$$

where

σ is conductivity at temperature T, σ_0 is constant, k_B is the Boltzmann constant and Ea is the activation energy. The activation energies E_a for $AgSbSe_2$ compounds, determined using an Arrhenius law, are close to another result obtained from electrical investigations (see Table 3). On the other hand, these data are little lower than the halve values of direct band gap energy E_g measured by optical method for intrinsic absorption region. It may suggest that results of electrical investigations correspond rather to activation energy of extrinsic charge carriers, but another explanation of discrepancies may lay in significant differences in microstructure of samples (thin layer versus bulk polycrystalline material).Figure.3 represents the variation of conductivity versus inverse of absolute temperature with various thicknesses for *$AgSbSe_2$*films. It is observed that conductivity increases with increase in temperature . It is clear from this figure that there are two activation energy and hence two transport mechanism for *$AgSbSe_2$*with different thicknesses. According to Davis and Mott model 1979[22] the tails of localized states should be rather narrow and extend a few length of tenths of an electron volt into the forbidden gap, and further more thus suggested of localized levels near the middle of the gap. This leads to different channels of conduction: Ea_1 is the activation energy required to transport electron from Fermi level to the extended states above the conduction band edge, Ea_2 is the activation energy required to transport electron from Fermi level to the localized below the conduction band edge . The increasing of thickness has no effect of the number on transport mechanisms of the system *$AgSbSe_2$*.The variation of Ea for as -deposited *$AgSbSe_2$* thin films with thickness are given in table 3. It is clear from this table that the activation energies decrease with the increase of film thickness. Indeed E_{a1} decreases from (0.719 to 0.476) eV when the thickness increases from 100nm to 700nm, while, also E_{a2} decreases from (0.178 to 0.0974) eV with the increase of thickness in same range. The decreasing of activation energy with the increase of thickness is resulting from the effect of reduction of energy gap and in turn reduces the energy requires to transport the carriers from Fermi level to the conduction band. The decrease of activation energy is due to structure improvement hence the increase of thickness led to phase transformation from amorphous to polycrystalline .

Table (3) D.C. conductivity parameters for as deposited $AgSbSe_2$ films with different thicknesses

Thickness (nm)	$\sigma_{R.T}(\Omega.cm)^{-1}$	Temp.Range (K)	Ea_2 (eV)	Temp.Range (K)	Ea_1 (eV)
100	$1.07x10^{-6}$	353-473	0.719	293-353	0.178
300	$2.67x10^{-6}$	353-473	0.693	293-353	0.138
500	$2.86x10^{-5}$	353-473	0.620	293-353	0.113
700	$11.6x10^{-5}$	353-473	0.476	293-353	0.097 4

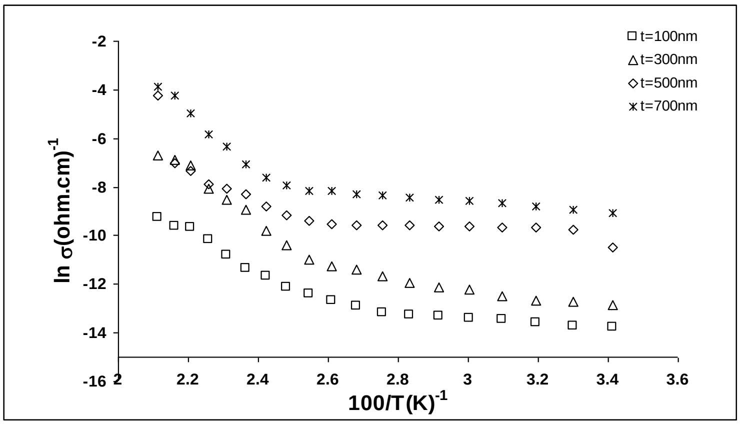


Figure (3) Variation of Ln(σ)(ohm.cm)$^{-1}$ versus 1000/T for as deposited $AgSbSe_2$ films with different thickness.

Conclusions

Increase of thickness has significant effect o n the structure of *$AgSbSe_2$* thin films. There are two conduction mechanism through out the D.C conductivity take place of *$AgSbSe_2$* for low thickness. Increase of thickness improve the structure of the prepared thin films which reflects as phase change from amorphous to polycrystalline structure but has no effect on the number of transport mechanisms take place in mention temperature range.

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