Effect the Thickness on Structural and Optical Paramteres of PbSe Thin Films

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ABSTRACT *PbSe compound have been successfully prepared by putting the propagate weigh of lead and selenium in sealed evacuated quartz tube under vacuum pressure (10-2Torr) in an oven at 1273 K for five hours. Thin films of PbSe of different thickness (300,500,700 and 1000 nm) have been prepared on KBr substrates at room temperature by vacuum deposition. The structure of PbSe alloy and thin film of different thickness are identified by X-ray diffraction. The structural parameters such as interplanar distance (d), grain size (D), and dislocation density (δ) have been evaluated. The optical properties have been studied in the range of wavelength range (2500-5000) nm. Measurements shows that the optical energy gap decrease from (0.290 to 0.245 eV) with the increase of thickness, the optical constants indicate significant variation with thickness increment.*

1. Introduction

Narrow band gap IV–VI lead salt semiconductors like PbTe, PbSe, and PbS and their ternary and quaternary alloys such as PbSnSe, PbSnTe, PbSrSe, and PbSnSeTe have been widely used in various solid state mid infrared devices, such as light emitting devices (LEDs), laser diodes (LDs), detectors, and thermoelectric generators. The IV–VI compounds predominantly crystallize in the rock-salt structure and its physical and electronic properties differ strongly according to the tetrahedral bonded structure. In addition, the lead salt compounds are mechanically much softer than their tetrahedral bonded counterparts and as a result easy plastic deformability has significant implications for device fabrication processes. IV-VI semiconductors have direct band gap and the conduction and valence bands of PbSe are quite similar, so that electrons and holes have comparable masses [1, 2].

2. Experimental work

Glassy alloy of PbSe are prepared by quenching technique. The exact proportions of high purity (99.999%) (Pb,Se) elements, in accordance with their atomic percentages, are weighed using an electronic balance with the least count of (10^{-4} gm). The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 15 cm and internal diameter ~ 0.8 cm). The ampoules containing where material are heated to 1273K and let at this temperature for 5 hours. The temperature of the furnace was raised at a rate of 3-4 °C/min. During heating the ampoules are constantly rocked .This is done to obtain homogeneous glassy alloys. After that they obtained melt was rapidly quenched in to water. The film structure is markedly influenced by deposition parameters such as substrate, composition and its surface structure, source and substrate temperatures, deposition rate, composition and pressure of the residual gases. A polycrystalline PbSe thin films with (different thickness (300,500,700 and 1000nm) were prepared using thermal evaporation by continuously feeding the material with a powder to a heated molybdenum boat of melting point about 1000 °K at this temperature instantaneous evaporation of the material will take place. Corning glass slides substrates were used, 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, rate of deposition (4-6A/sec), substrate temperature (room temperature). X-ray diffraction is a powerful non-destructive method for material characterization, by which the crystal structure, orientation, and grain size can be determined. The characterization is usually carried out with a typical X-ray wavelength that is comparable to the inter-atomic

distance in a crystal. In terms of the path difference Δs, constructive interference occurs when Δs is an integral multiple of the wavelength λ. Thus scattered beams emerge only when the condition is met by a family of crystal planes, where m is an integer. This is the Bragg condition for diffraction. The intensity of the reflected beam has sharp peaks in the corresponding directions. They are called Bragg peaks. The Bragg peak can be found by varying the angle 2θ of the detector [3].

$$2d \sin \theta = m\lambda \tag{1}$$

The full width at half maximum (FWHM) of the peak, Δ (2θ) (in radians), is a measure of the grain size (D), in a polycrystalline film, as described by Scherer's formula [4]:

$$b = \frac{0.89 \lambda}{\Delta(2\theta).\cos(\theta)} \tag{2}$$

Where θ is the Bragg angle. The source of radiation was Cu (k_a) with wavelength (l) equal to 1.5406A°. The dislocation (δ) of the samples can be determined from the equation [4]:

$$\delta = 1/D^2 \tag{3}$$

The optical properties measurements of binary system thin films deposited on single crystal KBr which includes the transmittance and absorbance spectra are studied over the wavelength range (2500-5000) nm by using FT-IR recorder spectrometer model Shimadzu. The optical energy gap E_g^{opt} of the PbSe prepared at different thickness t are measured throughout plotting $(\alpha h\nu)^{1/r}$ and (hν) the intercept on (hν) axis when $(\alpha h\nu)^{1/r} = 0$ is the optical energy gap. The optical constants represented by the refractive index (n), extinction coefficient (k), and dielectric constants (the real ε_r and imaginary ε_i) are calculated for the quaternary thin films using Eqs. [(4), (5), (6) and (7)] respectively [5.6]:

$$n = \sqrt{\frac{4R}{(R-1)^2} - k^2} - \frac{(R+1)}{(R-1)} \tag{4}$$

Where n is the real refractive index.

$$k = \frac{\alpha\lambda}{4\pi} \tag{5}$$

where α is the absorption coefficient and λ is the wavelength.

The real part of dielectric constant which represents the polarization term (ε_1) and imaginary part of dielectric constant

(C_2) can be calculated from the equations[6] :

$$\epsilon 1 = n2-k2 \qquad (6)$$

$$\epsilon 2 = \sqrt{2nk} \qquad (7)$$

3. Results and Discussion
3.1 X-ray diffraction
Fig. 1 shows X– ray diffraction of PbSe films prepared with different thickness, it is evident that all the prepared films have polycrystalline structure.
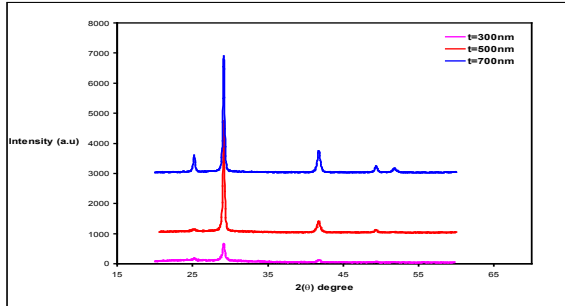

Fig. 1 X– ray diffraction of PbSe films prepared with different thickness.

Table 1 Structural parameters of PbSe thin films.

Thickness (nm)	hkl	d(Å) exp.	2θ	FWHM (β)	Grain Size(D) Å	Dislocation Density (δ) x10^5 A°
300	200	3.05985	29.1686	0.3814	101.470	9.71
	111	2.16200	25.2504	0.5376	77.199	16.77
	220	3.52360	41.7582	0.3689	105.190	9.036
500	200	3.05912	29.1686	0.310	124.100	6.8
	111	2.16135	25.2504	0.460	100.800	10.1
	220	3.52423	41.7582	0.321	185.500	3,1
700	200	3.05912	29.1686	0.2678	144.910	4.762
	111	2.16135	25.2504	0.4190	127.780	6.124
	220	3.52423	41.7582	0.3091	285.100	1.230

3.2 The Optical Properties of PbSe Films
The optical properties of the deposited PbSe films on single crystal KBr at R.T for different thickness (300,500,700, and 1000nm) have been determined by using FTIR transmittance and absorbance spectrum in the region (2500-5000nm). The reflectance spectrum has been measured. Also the energy gap and optical constants have been determined.
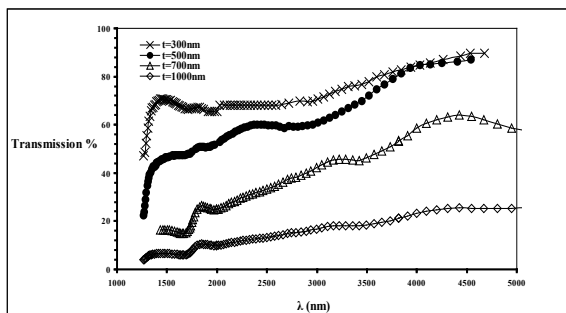

Fig.2 Transmittance spectra of PbSe thin films deposited at different thickness.

In general, we can observe from Fig. 2 that transmittance decreases with increasing of thickness which means an increase in the reflection and absorption. The shifts of transmittance toward lower energies accompanied the thickness increment explained according to the fact that increasing of thickness approaches structure of the samples from bulk material which reflects the shifting of the absorption edge toward lower energies values as will be seen in the next section.

3.3.1 The Optical Energy Gap
The optical energy gap values E_g^{opt} for PbSe films have been determined by using Tauc equation [7]:

$$\alpha h\nu = B(h\nu - E_g)^r \quad \ldots\ldots\ldots (4)$$

which is used to find the type of the optical transition by plotting the relations of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{1/3}$, $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^2$ versus photon energy (hv) and selecting the optimum linear part. It is found that the relation for r =2 yields linear dependence. The extrapolation i.e. E_g^{opt}, of the portion at $[(\alpha h\nu)^2 = 0]$ is shown in Fig.(3). The value of the optical energy gap reveals a decrease with the increase of thickness(t), moreover E_g^{opt} decreases from 0.30eV to 0.24eV when t increases from 300 to 1000nm ,this is can be explained as follows. It is well know that E_g^{opt} value of bulk material is lower than that of film sample, thus the increase thickness causes the reduction of E_g^{opt} values since the structure will be approach from that of bulk material.
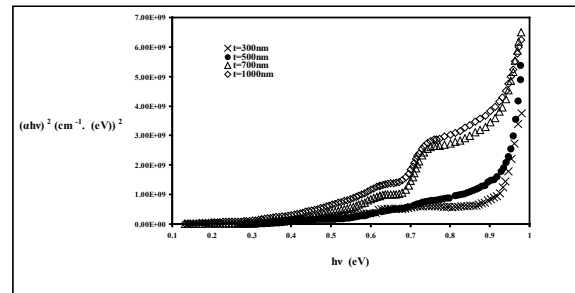

Fig. 3 Variation of $(\alpha h\nu)^2$ with (hv) of PbSe thin films deposited at different thickness.

3.3.2 Refractive Index
The variation of the refractive index versus wavelength in the range (2500-5000) nm, for PbSe films with different thicknesses (300,500,700,and 1000nm) prepared at R.T is shown in Fig.(4). We can notice from this figure and Table 2 that the refractive index, increases with increasing of thickness t for prepared samples, moreover n decreases from 2.41 to 2.21 for as deposited PbSe films when t increases from (300 to1000) nm, this behavior can be explained on the basic of that increasing of (t) to make PbSe more dense (increasing the packing density) which in turn decreases the propagation velocity of light through them which resulting in increasing of n values since n represent the ratio of light velocity through vacuum to velocity through any medium, also this behavior can be explained depending on the fact that refractive index value of bulk material exceeded that of thin film [8].
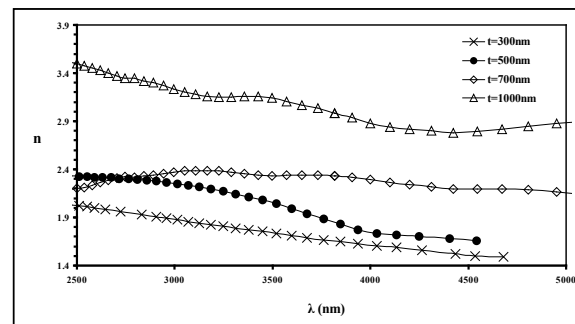

Fig. 4 Variation of n with wavelength of PbSe thin films deposited at different thickness.

3.3.4 Extinction Coefficient
The behavior of the extinction coefficient of PbSe films for different thicknesses, are shown in Figs.5. We can observe from this figure and Table 2 that the extinction coefficient increases with increasing of thickness for all films. It is clear that for as deposited PbSe films k increases when t increases from (300 to1000) nm, the behavior explanation is the increases of t increases the absorbance or the absorption

coefficient and consequently k will be increases, on the other hand this may be attributed to the same reason mentioned previously in the refractive index, since the increasing of thickness decreases the optical energy gap as a result of absorbance increment [9].
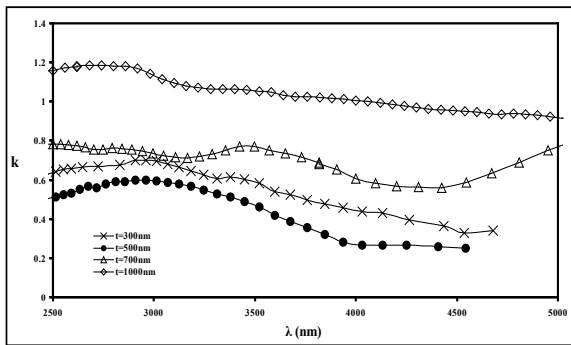

Fig.5 Variation of k with wavelength of PbSe thin films deposited at different thickness.

3.3.5 The Dielectric Constants (e_r and e_i)

The variation of the real (e_r) and imaginary (e_i) parts of the dielectric constant values versus wavelength in the range (0.2–1.1)mm for PbSe films deposited at R.T with different thicknesses (300,500,700,and 1000nm) , are shown in Figs. (6 and 7). The behavior of e_r is similar to that of the refractive index because of the smaller value of k^2 compared with n^2 according to equation 6, while e_i is mainly depends on the k values. It is found that e_r increases with increasing of thickness. Moreover e_r found to increase from 5.8 to 7.39 for as deposited films when thickness increases from (300 to 1000) nm, as shown in Table 2.

The imaginary part of dielectric constant e_i reveals the same behavior of e_r with thickness. It is clear from Table 2 that e_i for as deposited PbSe films increases from 0.021 to 0.0299 when t increases from 0.3 to 0.7mm .The same explanation of n and k can be given to e_r and e_i [9,10] .
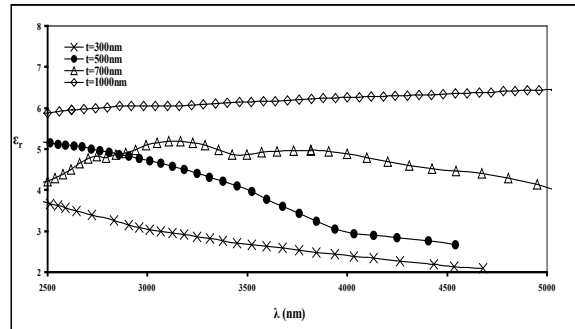

Fig.6 Variation of e_r with wavelength of PbSe thin films deposited at different thickness.

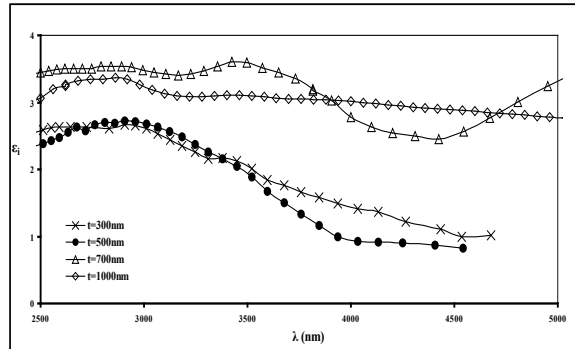Fig.7 Variation of e_i with wavelength of PbSe thin films deposited at different thickness.

Table 2 The values of n, k, $\in_1$, $\in_2$, T at λ=3500 nm, and E_g^{opt} for PbSe thin films with different thickness.

Thickness (nm)	n	k	$\in_1$	$\in_2$	T	E_g^{opt} (eV)
300	1.733	0.58	2.664	2.118	0.76	0.290
500	2.043	0.46	3.963	2.014	0.68	0.314
700	2.335	0.769	4.861	3.593	0.45	0.280
1000	3.14	1.058	6.131	3.106	0.18	0.245

4. Conclusions

The prepared PbSe alloys and films have polycrystalline structure and significant effect of the proffered plane for crystal growth (111). PbSe become more opaque with the increasing of thickness.

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