Impact of various irradiation photon energies and gamma doses on the optical properties of ZnSe nanostructure thin film

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Abstract ZnSe thin films were prepared by thermal evaporation technique under high vacuum (10^{-6} Torr) at 300 K and different film thickness. The structure of thin films was measured using grazing incident in-plane X-ray diffraction (GIIXD) and shows single phase zinc blende structure. The particle sizes of the deposited films were estimated for low film thickness by TEM and high film thickness by GIIXD. The particle size of ZnSe films was decreased from ∼8.53 to 3.93 nm as film thickness lowered from 200 to 20 nm which ensures the nanocrystalline structure. The optical transmission (T) and reflection (R) in the wavelength range 190–2,500 nm for irradiated and unirradiated ZnSe thin films under investigation were measured. The effect of irradiation of different energies in range (0.1–1.25 MeV) from X-ray, ^{137}Cs and ^{60}Co irradiation sources were studied for ZnSe thin films of 100 and 200 nm thicknesses. The dependence of the absorption spectra and refractive index were investigated for different energies irradiation sources. The ZnSe films show direct allowed interband transition. The effect of particle size of nanocrystalline ZnSe thin films for unirradiated and irradiated by gamma (γ) doses from ^{137}Cs on the optical properties was studied. Both the optical energy bandwidth and absorption coefficient (α) were found to be (γ) dose dependent.

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1 Introduction

ZnSe is an II–VI compound semiconductor with a direct optical band gap of 2.7 eV at room temperature [1], which makes it suitable material for a variety of the optoelectronic applications in the blue green wave length region, including light emitting diodes and high power laser windows [2]. It is also used as window material in high efficiency solar cells, because its large band gap permits a large number of photons to reach the absorber layer [3].

ZnSe nanostructure as a wide band gap semiconductor compounds have received much attention for the application in optoelectronic devices, such as blue laser diode, light emitting diodes, solar cells and IR optical windows [4].

Theoretical physics described interaction of radiation with matter as a collision of photon of γ-ray with an electron in the valance band caused the ejection of the electron from the atom. The main interaction mechanism with matter and the effects of γ-ray on the material properties are depending on radiation energy, radiation energy distribution and doses.

Examining the impact of γ irradiation of different energies and X-ray irradiation of the ZnSe thin films as ionizing radiation (high energy photon) opens the new way for the study of fast transient phenomena such as energy transfer, energy storage, excitation and de-excitation processes in optical materials.

Generally the physical properties of semiconductor compounds may change by irradiation of gamma doses [5–7]. The variation of the semiconductor band gap width will be changed as a result of radiation effects. This phenomenon could be important in using the ZnSe films in various devices.

The aim of this work is to study the exposure effect of various photon energy sources: 100 keV, 0.266 MeV and 1.25 MeV on the optical energy band width and absorption coefficient (α) of ZnSe thin films of different nanoparticles. The impact of the different γ-radiation doses from ^{137}Cs on optical properties of ZnSe nanostructured thin films was also examined.

2 Experimental

The ingot powder of ZnSe have been synthesis by solid solution method under temperature of $1,000 \pm 10$ °C at high vacuum (10^{-6} Torr) in silica tubes using high purity elements 99.999% of zinc and selenium. This powder were used to prepare ZnSe thin films by thermal evaporation technique using Edward coating unit E-306 under vacuum of 10^{-6} Torr at 300 K over freshly well cleaned glass substrates. The thickness of all investigated films was measured by the film thickness monitor (Edwards FTM5) attached with vacuum chamber. The internal structure for ZnSe thin films were examined by grazing incident in-plane X-ray diffraction (GIIXD) technique using Philips X'Pert diffractometer system of generating setting was 40 kV/40 mA with CuKα radiation source. The grain or particle size of the prepared films was determined by TEM (Joel-1230, Japan) for low thickness films and by GIIXD for films of 100 and 200 nm thickness.

The effect of radiation on ZnSe films was examined by exposing ZnSe films to different photon energy sources from X-ray machine, ^{137}Cs γ-ray and ^{60}Co γ-ray. The number of photons transmitted after exposure through ZnSe thin film depends mainly on the film thickness and the energy of the individual sources.

The X-ray and γ-ray doses were measured using secondary standard dosimetry system at (NIS) with a combined uncertainty $\pm 2\%$ which is considering the reference dosimetry system. Three groups of samples were exposed to radiation sources under reference conditions.

First group, ZnSe thin film of thicknesses (100 and 200 nm) was irradiated by X-ray at (100 keV, 5 mA) from X-ray Philips-232Machine. Second group, ZnSe thin film of thicknesses (100 and 200 nm) were irradiated by gamma radiation from ^{60}Co-source (1.25 MeV) where the dose rate is 3 Gy/h measured at reference conditions and also irradiated by ^{137}Cs source (0.662 MeV). Third group, ZnSe thin films of thickness ranging (20–120 nm) were irradiated by different gamma doses ranging (0.5–34.5 Gy) from ^{137}Cs source.

The optical transmission and reflection of all films before and after irradiation was recorded using (Jasco V-570) spectrophotometer in the wavelength range from 190 up to 2,500 nm. The measurements were carried out at room temperature at ambient atmosphere with an error of 1%.

3 Results and discussion

Grazing incident in-plane X-ray diffraction (GIIXD) is an X-ray scattering technique penetrate only a few nanometer in depth, through which the in-plane lattice parameter and lattice orientation of thin surface of the deposited ZnSe films can be determined [8, 9].

The structure of unirradiated ZnSe thin film of thickness 100 and 200 nm has been measured by grazing incidence in-plane X-ray diffraction (GIIXD). The GIIXD patterns for unirradiated thin films of ZnSe prepared by thermal evaporation technique are shown in Fig. 1. The main three strongest lines for ZnSe film of orientations (111), (220) and (311) of cubic zinc blende (zb) single phase are observed in thin films of thickness 100 and 200 nm under investigation which matched to that of (zb) ZnSe crystals international card (a = 5.66882 Å; ICCD Card No. 37-1463). The Miller-indices (hkl) for two patterns are indicated in Fig. 1a, b. The structure of the ZnSe films were examined after exposure to irradiation sources of different energies (X-ray, ^{137}Cs and ^{60}Co) using GIIXD and there is no change in crystalline structure was detected.

The crystallite or particle size (P$_s$) of the films of 100 nm and 200 nm was determined from the GIIXD pattern using line (111) by using Scherrer equation [10]:

$$P_s = \kappa\lambda/\beta \cos(\theta) \tag{1}$$

where κ is constant known as shape factor and it is taken as $\kappa \approx 1$, λ is the wavelength of the X-ray radiation employed, β is the angular half width at half the peak height and θ is the Bragg's angle. For accurate estimation of the crystallite size (D) the following equation is applied [11]:

$$\beta = \Delta B = \sqrt{B_f^2 - B_Q^2} \tag{2}$$

where ΔB is the increase of the line width B$_f$ is the experimentally measured half width of the film under investigation, B$_Q$ is the measured half width of a line produced under similar conditions by a standard substance. The thin film of 100 nm thickness showed crystallite or particle size (P$_s$) 6.554 nm in nano range and the 200 nm thickness film has (P$_s$) 8.527 nm using Eq. 1. It could be noted that the particle size of ZnSe of 100 nm thickness was also estimated from the TEM micrograph have shown particle size (P$_s \approx 6.5$ nm) as seen in Fig. 2. The structure and particle size of all ZnSe films of thickness t $\leq$ 120 nm were determined by transmission electron microscope (TEM). The TEM diffraction patterns ensured single phase

(a)

(b)
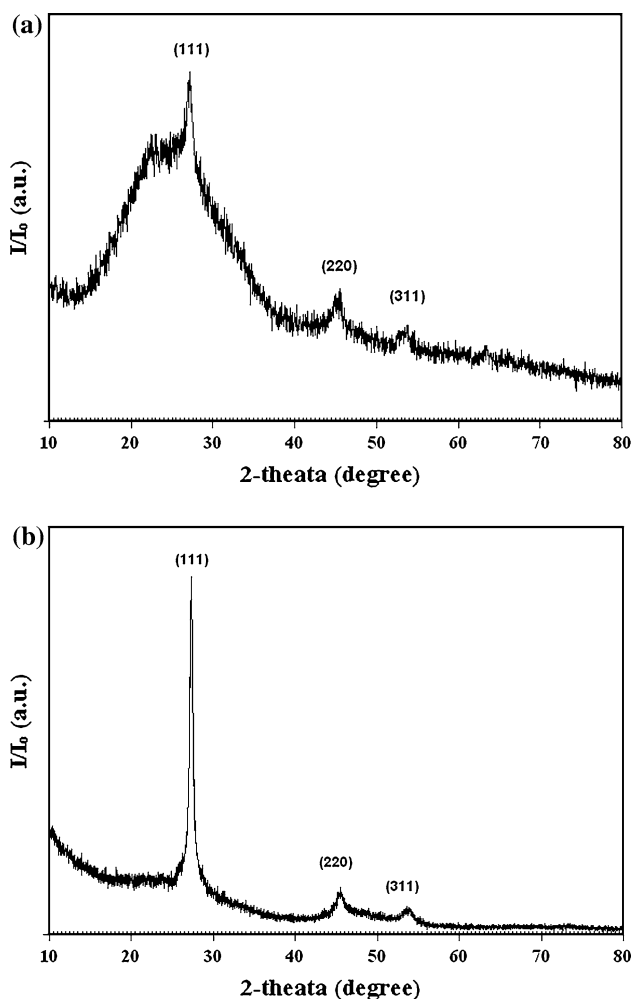
Fig. 1 Grazing incident in-plane X-ray diffraction pattern for ZnSe thin film of thickness **a** 100 nm and **b** 200 nm
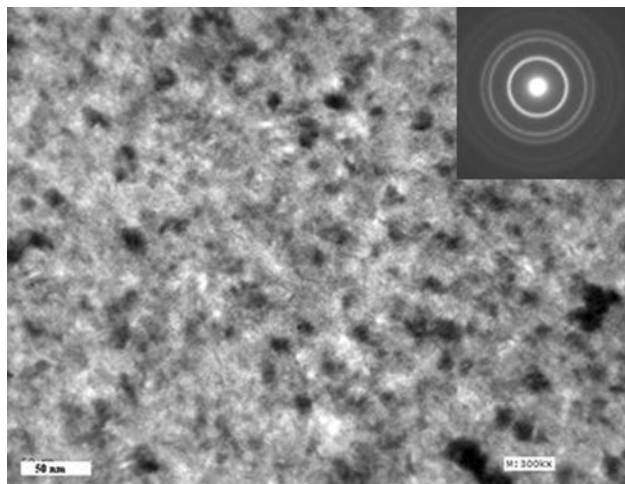
Fig. 2 TEM micrograph of unirradiated ZnSe thin film of thickness 100 nm. The diffraction pattern is *inserted*

cubic Zinc blende nanocrytalline structure. The average particle size that determined by TEM micrographs has values of 3.9, 5.3, 6.1, 6.5 and 6.9 nm for 20, 50, 80, 100 and 120 nm film thickness, respectively. It could be noted that for films of thickness 100 nm, a slight difference of the estimation of particle size which is 0.054 nm is observed by evaluation using XRD patterns applying Eq. 1 and by using TEM micrograph. It was reported that physical properties of the films are influenced by its particle size for nanostructured materials [12]. In particular the optical constants and the optical band gap are dependent on the particle size of the nanostructured thin films.

The optical transmission and reflection as a function of wavelength from 190 up to 2,500 nm were measured for unirradiated and irradiated ZnSe films of $P_s \approx 6.5$ and $P_s \approx 8.5$ nm by different photon energies from the sources (X-ray and γ-ray from ^{137}Cs and ^{60}Co). The optical absorption coefficient was calculated from the optical transmission and reflection spectra using the following equation [13]:

$$T = (1 - R)^2 e^{-\alpha t} \tag{3}$$

where T is the transmission, R is the reflection, α is the absorption coefficient and t is the film thickness.

The plots of $Ln(\alpha)$ versus photon energy E for film particle size $P_s \approx 6.5$ nm and $P_s \approx 8.5$ nm before and after irradiation from different energy sources was indicated in Fig. 3a, b. When energy emitted from radiation source hitting the material which having specific energy band gap, the electronic structure changed by absorbing electrons of these quantized energies and go to another states in unstable positions which called defect states lie in the band gap of the material and showing a hump in the absorption tail spectra. As the nanostructured material in general having energy gap depending on its particle size so the position of the defect state could be changed with the band gap and consequently the particle size. It could be observed from Fig. 3 that the hump in the absorption tail spectra for high particle size ($P_s = 8.527$ nm) is shifted towards the lower energy side than that of lower particle size ($P_s = 6.554$ nm). These humps at low energy values are due to defect states caused by irradiation processes and mainly dependant on the structure and particle size of individual ZnSe films.

The optical band gap E_g is calculated according to the relation [4, 13, 14]:

$$\alpha(E) = \beta(h\nu - E_g)^n \tag{4}$$

where n varies according to the type of the optical transition. The best linearity is obtained for n = 1/2, i.e. for allowed direct transition. The optical energy gap was calculated for unirradiated and irradiated thin films with different energy sources and listed in Table 1.

Fig. 3 Absorption spectra for unirradiated and irradiated ZnSe thin films of thickness **a** 100 nm and **b** 200 nm by different photon energies
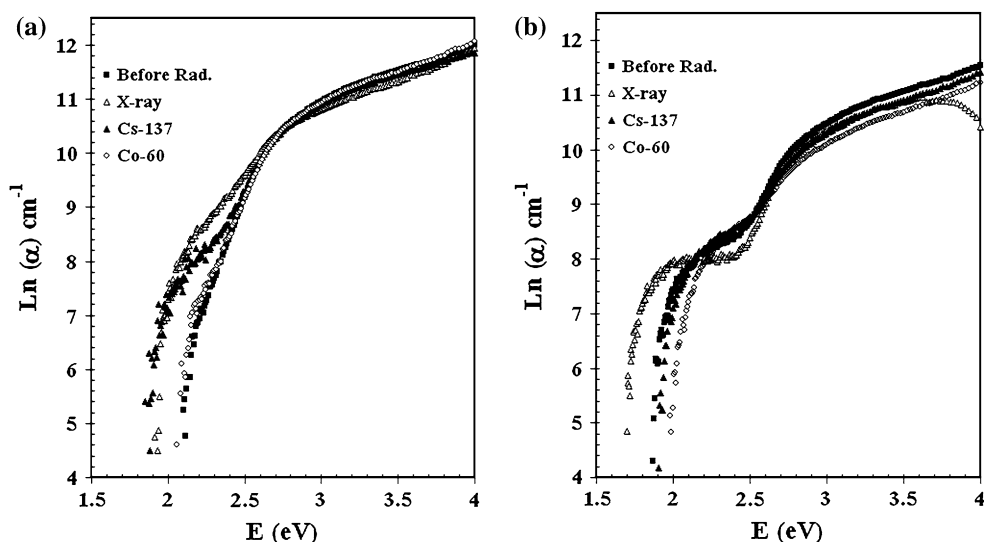
Table 1 The band tail width and optical energy gap for films of $P_s = 6.554$ nm and $P_s = 8.527$ nm before and after irradiation

Film condition	Band tail width E_o (eV)		E_g (eV)	
	6.554	8.527	6.554	8.527
P_s (nm)	6.554	8.527	6.554	8.527
Before radiation	0.115	0.167	3.8	3.65
Irradiated by X-ray (0.1 MeV)	0.188	0.171	3.7	3.1
Irradiated by ^{137}Cs (0.662 MeV)	0.160	0.200	3.4	3.6
Irradiated by ^{60}Co (1.25 MeV)	0.135	0.250	3.6	3.6

It could be observed from Fig. 3a, b by decreasing the energy of the irradiation source 1.25, 0.662 and 0.1 MeV, the hump at absorption tail is shifted towards the lower energy side. The band tail width E_o (eV) [15] before and after irradiation for $P_s = 6.554$ nm and $P_s = 8.527$ nm were determined from Fig. 3 and listed in Table 1.

It could be noted that the optical energy gap have generally lower values after irradiation to gamma sources and the band tail width increases as influenced by the defect states. The X-ray source was consider as a weak or soft energy source which may affect the surface layers only this could show that the effect of X-ray is clear on band tail width in the low particle size films where the surface to volume ratio is very high than that for films of higher particle size.

The refractive index as a function of photon energy was calculated from the reflection spectra [13]. Figure 4 shows the refractive index as a function of wavelength for film of particle size (a) $P_s = 6.554$ nm and (b) $P_s = 8.527$ nm. It could be observed that the exposure to irradiation sources of different energies affects refractive index values for higher particle size film than lower one as the thick layer which cause a clear effect due to condensation of the material. The low particle size film has very slight change

of the refractive index values as it has very thin layer which its condensation nearly does not affected. Figure 5a, b shows the refractive index as a function of irradiation photon energy for low and high particle size ($P_s = 6.554$ and 8.527 nm). It could be deduced from Fig. 5a that for low particle size films, the refractive index have nearly constant slight behavior with increasing irradiation photon energy. But the refractive index Fig. 5b has noticeable decreased with increasing irradiation photon energy for high particle size which indicates that the material becomes less condensed after irradiation. This could reflect more porosity in material of the irradiated films.

The optical transmission and reflection as function of wavelength for unirradiated and gamma irradiated (^{137}Cs) ZnSe films of thickness range from 20 to 120 nm were measured. The thin films irradiated by different gamma doses ranging from 0.5 up to 34.5 Gy.

The representative optical absorption coefficient spectra of examined films are shown in Fig. 6. It could be observed at the fundamental absorption region where at E > 3 eV that the γ-irradiation doses decrease the absorption values of the spectra which influenced the optical gap to have lower values. This decrease in the optical gap values depends on the particle size of the irradiated nanostuctured film. The effect of increases gamma doses may increase the density of broken bonds present in the semiconductor lattice.

The plot of $(\alpha E)^2$ against photon energy (E = hν) for unirradiated and γ-irradiated ZnSe nanostuctued films of thickness (20–120 nm) and P_s ranges from $\sim$3.9 to 6.9 nm were represented as in Fig. 7. The optical band gap E_g is determined and the inserted Fig's for illustrate the difference in optical band gap for irradiated sampled with different γ-doses. The values of E_g before and after γ-irradiation which determined from Fig. 7 is listed in

Fig. 4 The refractive index as a function of wavelength for unirradiated and irradiated ZnSe thin films of particle size P_s **a** 6.5 nm and **b** 8.5 nm by different photon energies
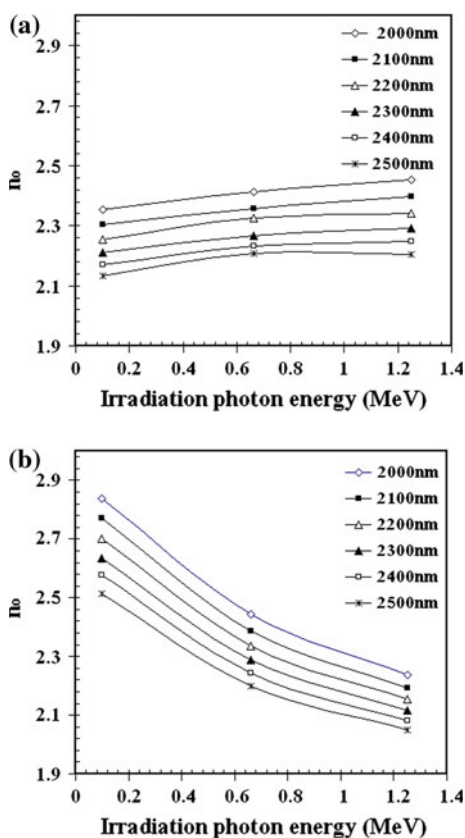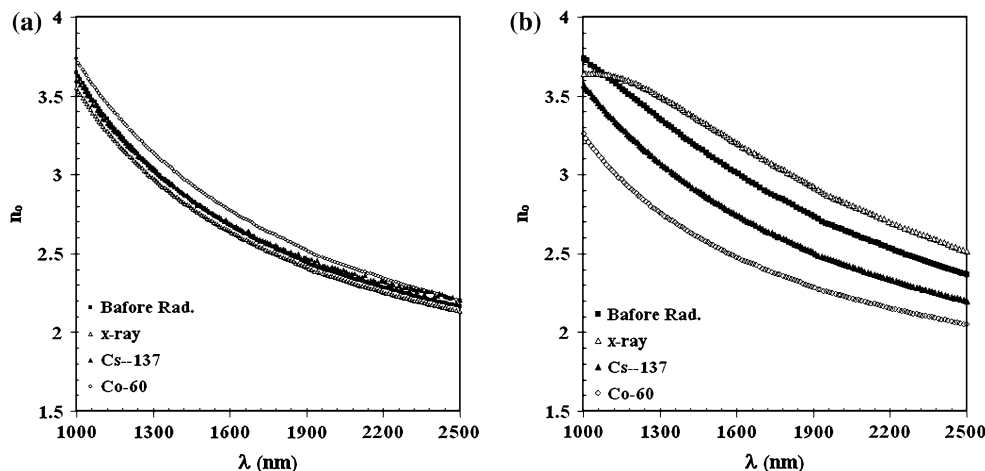
Fig. 5 The refractive index as a function of irradiation energy for different wavelengths for films of particle size P_s **a** 6.5 nm and **b** 8.5 nm

Table 2. From Table 2 the values of optical band gap E_g decrease for irradiated films with increasing γ-dose from 0.5 Gy up to 34.5 Gy for all films than its values of unirradiated thin films [16]. At high γ radiation doses, the accumulated radiation dose induced defect states appeared at absorption tails. This is probably manifested by a decrease in the band gap width. Mak et al. [17] discuss the maximum variation of the optical energy gap for γ-dose of

$\approx 10^2$ Gy for ZnSe single crystal. They recorded that, the band gap width of semiconductor materials decreased by increasing γ-irradiation.

The slope of the absorption edge for all films (Fig. 6) is influenced by the variation at the fundamental absorption region due to the reduction of optical band gap after irradiation and the defect states at the absorption tail at low energy values. This effect of increasing γ-irradiation doses on optical absorption depends on the particle size of the nanostructured film.

Figure 8 shows the relation between the value of the refractive index at 2 μm for unirradiated and irradiated films and the particle size of the deposited films. It could be noticed that at low particle size films there is no effect of different γ-doses, but starting from $P_s \sim 6.5$ nm the effect of doses decrease the refractive index. The values of refractive index n_o generally rise with increasing particle size up to 6.9 nm. The reflective index seems to be unaffected by γ-irradiation, especially for doses >0.5 Gy and tends to saturated values for films of P_s more than 6.5 nm. This is could be due to the effect of γ-irradiation on high thickness and particle size films is more clear in reducing refractive index values as it reflects decreasing the condensation of irradiated films.

4 Conclusion

Irradiation by different photon energies from X-ray, ^{137}Cs and ^{60}Co sources affects the optical properties of nanostructure ZnSe thin films The main three strongest lines for ZnSe film of orientations (111), (220) and (311) of cubic zinc blende (zb) single phase are observed in the unirradiated and irradiated ZnSe films. The TEM measurement ensured structure and showed the particle size P_s for ZnSe films of $t \leq 120$ nm to have nanocrystalline zinc blende structure of $P_s \leq 6.5$ nm.

Fig. 6 : Absorption spectra for unirradiated and irradiated of ZnSe thin films of particle size P_s **a** 3.9 nm, **b** 5.3 nm, **c** 6.1 nm, **d** 6.5 nm and **e** 6.9 nm
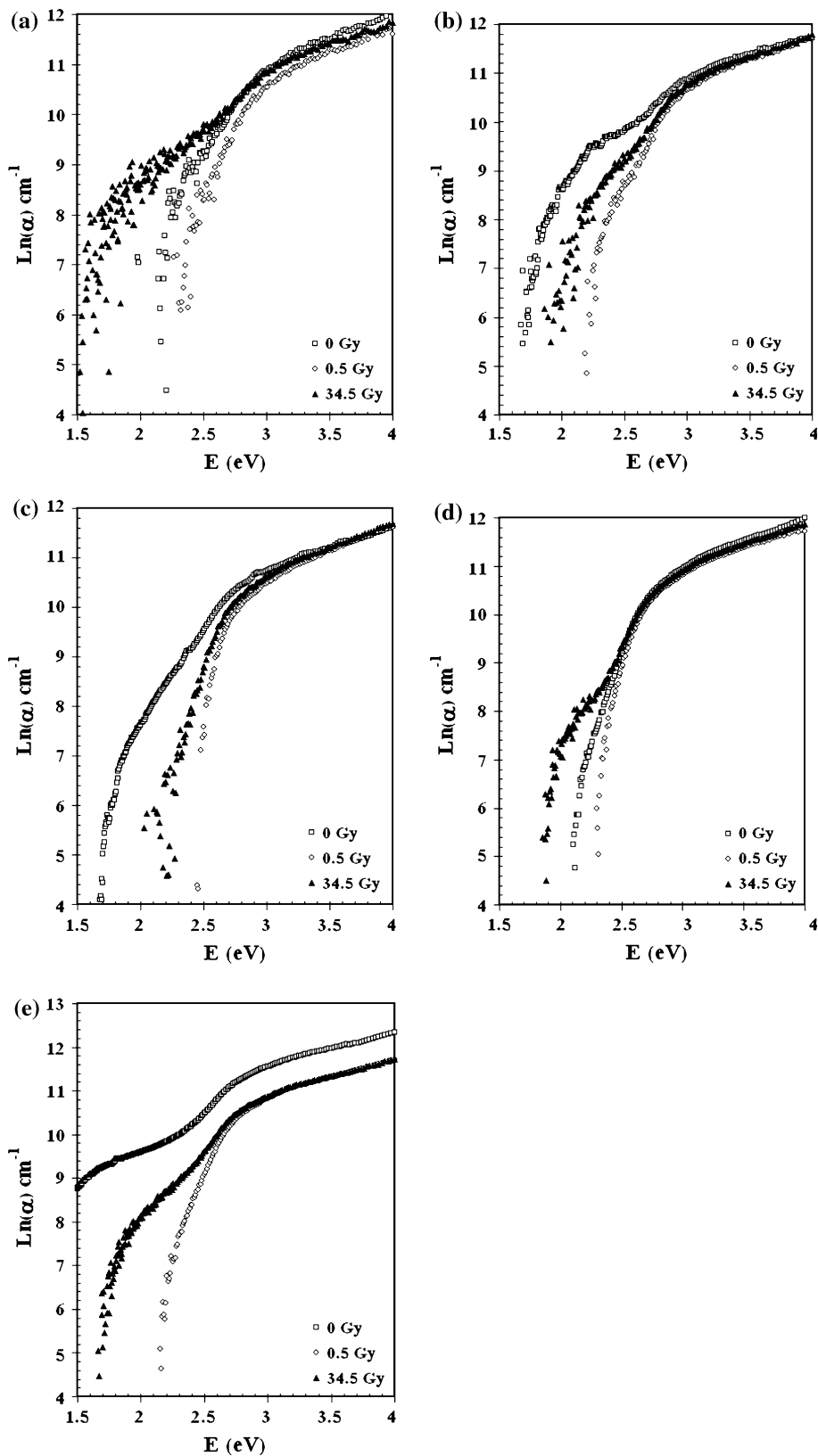
The optical energy gap E_g of films having particle size $P_s \approx 6.5$ and 8.5 nm generally decreased after irradiation from different energy sources. It was observed that a hump in the absorption tail spectra after irradiation for high P_s is shifted towards the lower energy side than that of small P_s. The refractive index for low P_s have a slight change but in

Fig. 7 Relation between
Energy and $(\alpha E)^2$ for
unirradiated and irradiated of
ZnSe thin films of particle size
P_s **a** 3.9 nm, **b** 5.3 nm,
c 6.1 nm, **d** 6.5 nm and
e 6.9 nm
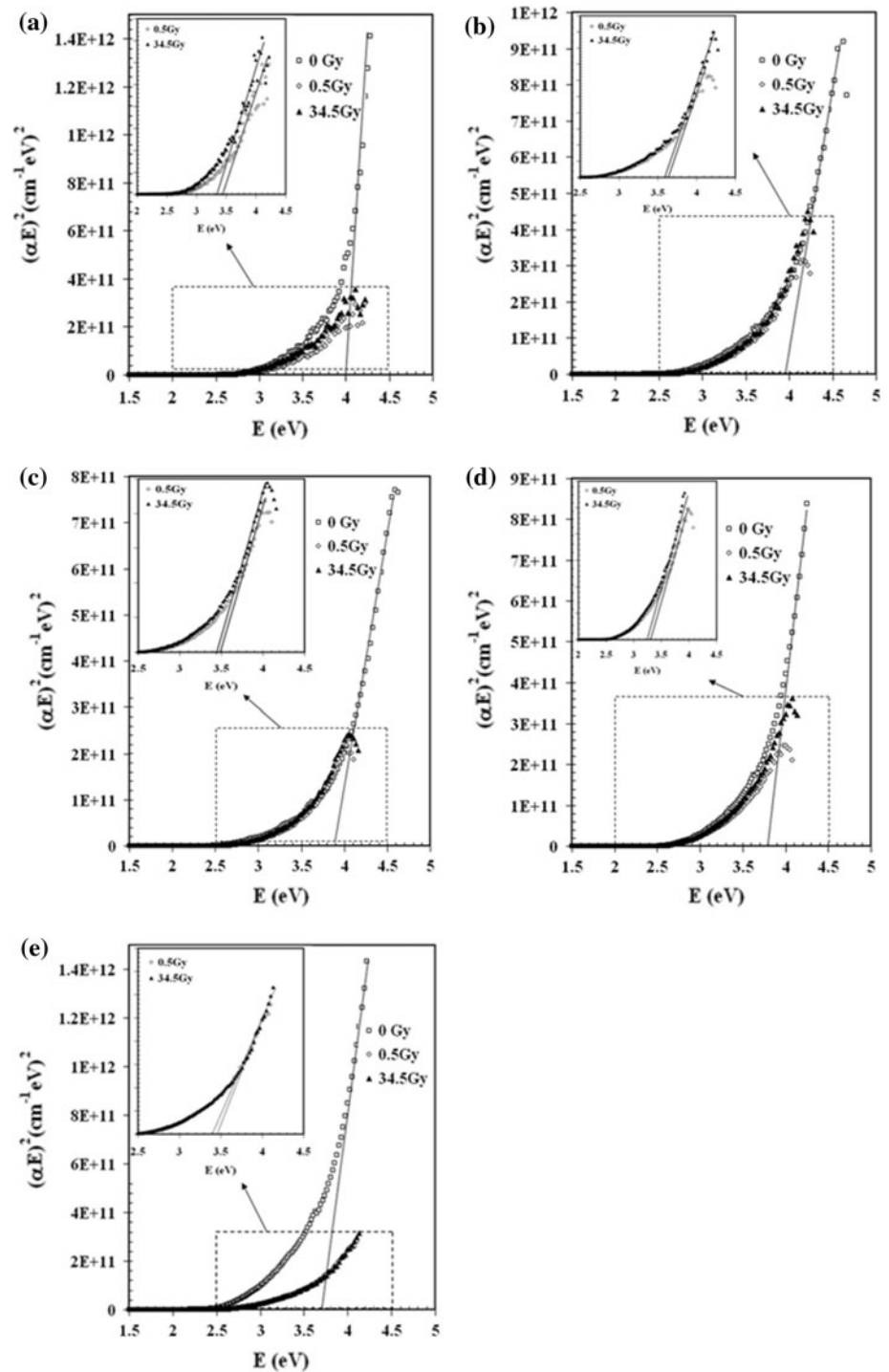
Table 2 The variation of
optical band gap before and
after γ-irradiation for film of
particle size P_s ranging from
(3.9 to 6.9 nm)

Dose Gy	Optical band gap E_g (eV)				
	$P_s = 3.9$ nm	$P_s = 5.3$ nm	$P_s = 6.1$ nm	$P_s = 6.5$ nm	$P_s = 6.9$ nm
0	4	3.95	3.90	3.80	3.70
0.5	3.45	3.65	3.50	3.30	3.45
34.5	3.35	3.60	3.45	3.24	3.40
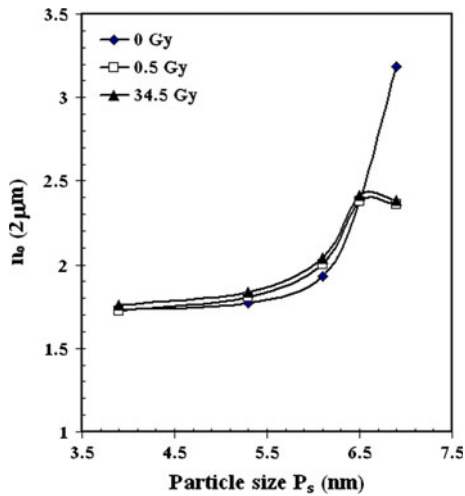
Fig. 8 The refractive index (n_o) at 2 μm as a function of the particle size (P_s) of ZnSe films before and after irradiation of 0.5 and 34.5 Gy γ-doses

high P_s the refractive index decreased by increasing irradiation photon energies. The refractive index shows constant values for low P_s values and decrease for high P_s values with increasing the energy of irradiation source.

The optical energy gap of nanocrystalline ZnSe decreases with increasing both the particle sizes and irradiation of γ-doses. The values of refractive index (n_o at 2,000 nm) generally rise with increasing particle size up to 6.9 nm then tend to more stable behavior.

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