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Effect of γ-irradiation on the optical properties of $AgGaSe_2$ thin films material deposited by e-beam evaporation technique

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Abstract

$AgGaSe_2$ thin film material has been deposited at room temperature by e-beam evaporation technique onto glass substrates at vacuum pressure of $\sim 1.8\times10^{-3}\,Pa$. The elemental chemical composition of the deposited films was confirmed using the energy dispersive X-ray analysis (EDX). The effect of gamma irradiation on the optical properties of the deposited films has been studied in the spectral range 550-2500 nm. The refractive index dispersion in the transmission and low absorption region is adequately described by the effective single oscillator model, from which the single oscillator parameters have been calculated as a function of gamma dose. The analysis of the optical absorption coefficient in the strong absorption region indicates the presence of both allowed direct transition in the photon energy range 1.602-2.03 eV, while a forbidden direct optical transition in the photon energy range 2.03-2.18 eV was observed. The energies of such optical transitions have been determined for different gamma dose. A variety of applications are discussed.

Key words: Thin film, $AgGaSe_2$, X-ray analysis, gamma irradiation, optical absorption coefficient, optical transitions.

INTRODUCTION

The chalcogenide glasses are one of the most widely known families of amorphous materials and have been extensively studied for several decades because of their interesting fundamental properties and because of their potential applications in optical imaging, optical recording and integrated optics, microelectronics and optical

communications. Most of these applications are based on the wide variety of light-induced effects exhibited by these materials (Ewen and Owen, 1992 ; Pfeiffer et al., 1991; Andriesh et al., 1986; Elliott, 1991). When these glasses are irradiated with high energy particles or light, bond breaking and bond rearrangement can take place, which result in the change in the local structure of the glassy materials. These include subtle effects such as shifts in the absorption edge (photo-bleaching and photo-darkening), and more substantial atomic and molecular reconfiguration such as photo-induced refractive index changes and photo-doping effects (Elliott et al., 1986; Tanaka et al., 1990). In general, these phenomena are associated with changes in the optical constants (Shimakawa, 1995; Frumar, 1997) and absorption edge shift (Matsuo et al.,2006). These light-induced changes are favoured in chalcogenide glasses due to their structural flexibility (low coordination of chalcogens) and also due to their high-lying lone-pair p states in their valence bands. In the last few decades, many potential applications based on light-induced effects have been explored, for example, in the fields of sub-micrometre, photo-resists, optical memories, diffraction elements, optical light-guide and optoelectronic elements and devices (Schunemann et al., 2000). Semiconductor optoelectronic devices can be operated under conditions of the action of different kinds of high energy radiation. The duration, intensity and energy of such radiations influence differently the parameters of these devices. Therefore, an establishment of the regularities in the changes in the device characteristics affected by radiation can be used for adjustment of their operating conditions.

$AgGaSe_2$ (AGS) is a well-known $I–III–VI_2$ semiconductor compound that crystallizes in the chalcopyrite structure (Shay and Wernic, 1975). The AGS thin films, with an optical band gap ≈1.8 eV, are a potential material for NIR applications as well as for the preparation of Schottky diodes and solar cells (Shay and Wernic, 1975; Murthy et al., 1991). The structure, optical and electrical properties of AGS thin film have been previously studied (Murthy et al., 1991; Bhuiyan et al., 2008; Soliman, 1995). However, to the best of the author's knowledge there is no work that concerning the effect of γ-irradiation on the optical properties of AGS thin films has reported.

In the present work we will addressed the effects of gamma irradiation on the optical properties of $AgGaSe_2$ thin films.

MATERIALS AND METHODS

Polycrystalline bulk ingot material of $AgGaSe_2$ was prepared by direct fusion (at ~1050 K) of a mixture of its constituent elements (high purity) in stoichiometric ratio, in vacuum-sealed silica tube, following controlled heating and cooling stages. A programmable electrical furnace has been used for this task.

$AgGaSe_2$ thin films were deposited at room temperature onto clean glass substrates using the previously prepared material via electron beam evaporation system (Type Leybold-Heraeus Combitron CM-30, Germany). The deposition rate was almost maintained constant during the evaporation process at nearly ~8 nm/s. The thickness

of the deposited film was monitored during evaporation process using quartz crystal thickness monitor (Type Edwards FTM5). The elemental chemical composition of the as-deposited film was determined by means of energy dispersive X-ray spectrometer (EDS), interfaced to a scanning electron microscope.

The transmittance *T*, and reflectance *R*, spectra of the as-deposited films and those subjected to different γ-doses at constant duration time were recorded at normal light incident in the wavelength range 550-2500 nm, using a double beam spectrophotometer (Type Jasco, V-570, UV-VIS-NIR). The optical measurements were carried out at room temperature one day after the film was exposed to γ-rays. Before and after optical measurements the samples were kept in dark desiccators. The optical measurements were carried out on various parts of the deposited films, scanning the entire sample and a very good reproduction of spectra was generally achieved. In the present work Co^{60} γ-cell (2000Ci) was used as a γ-rays source.

RESULTS

The compositional analysis of AGS film deposited at room temperature reveals that the elemental atomic composition of AgGaSe film was found to be 22.71:24.08:53.21, respectively, indicating nearly stoishiometry film with nominal composition $Ag_{0.908}Ga_{0.963}Se_{2.128}$. Fig.1 illustrates the EDS spectra of a typical representative sample of AGS films deposited onto clean glass substrate. Fig. 2 shows the transmittance and reflectance spectra of AGS films at different γ-doses.

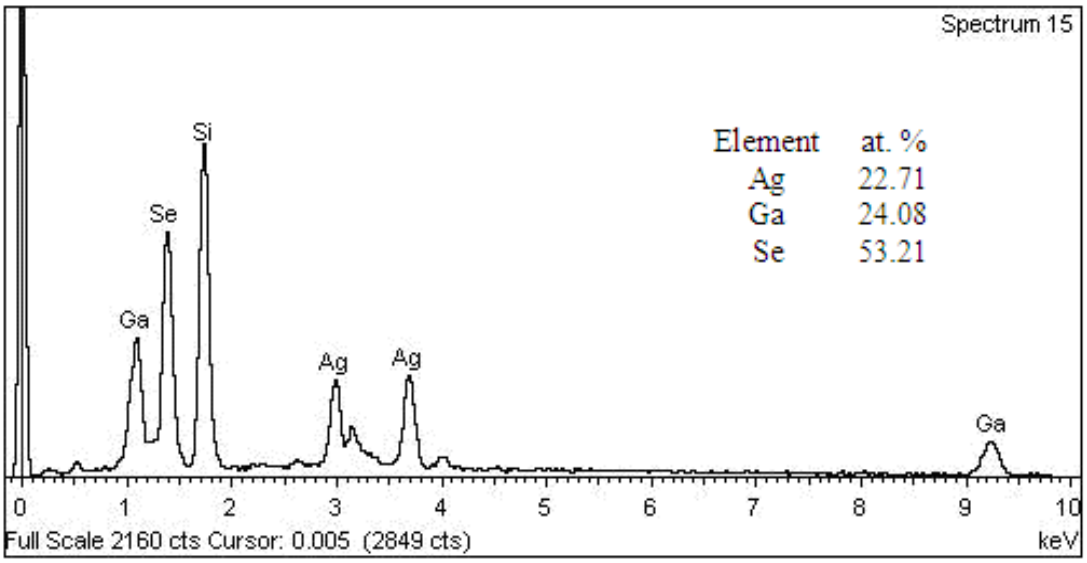

Fig.1 EDX spectra of $AgGaSe_2$ thin films

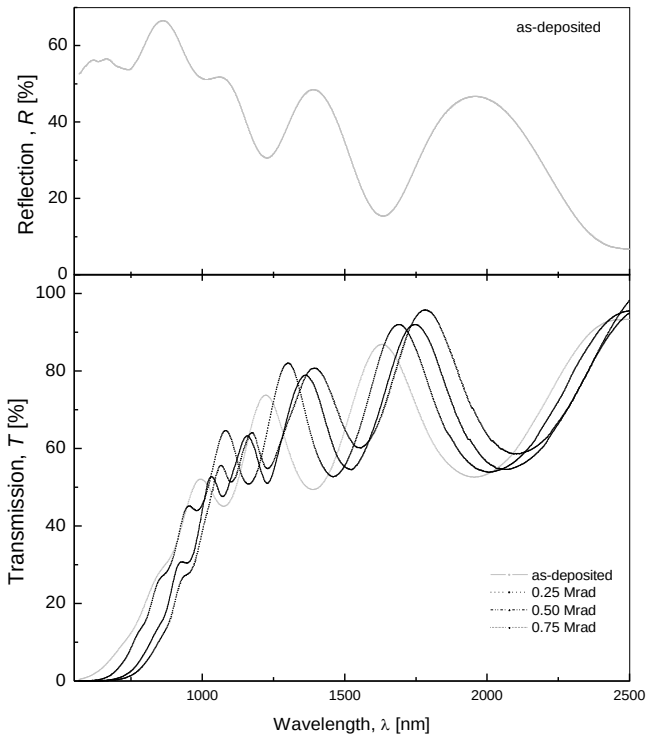

Fig.2 Transmission and reflection spectra of $AgGaSe_2$ films at different γ-dose.

Fig. 3 shows dispersion curves of the refractive index of AGS thin films at different γ-doses. Fig. 4 shows the induced absorption coefficient, μ as a function of wavelength and at different γ-dose.

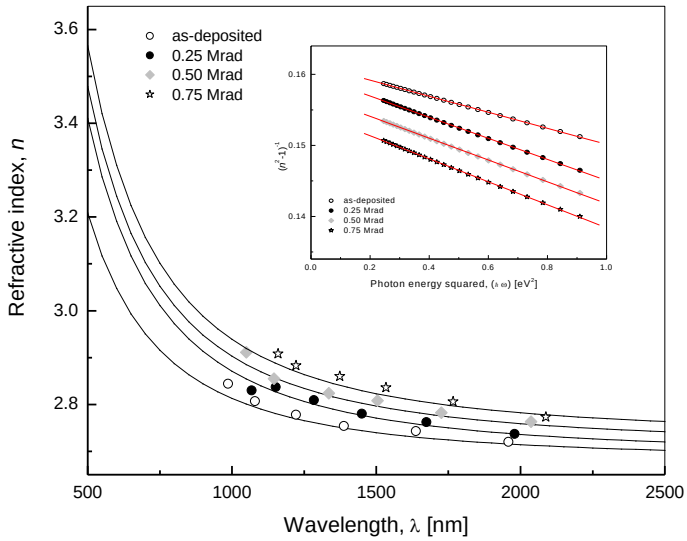

Fig.3 refractive index of $AgGaSe_2$ films at different γ-dose. Inset shows the plot of $(n^2-1)^{-1}$ vs. photon energy squared.

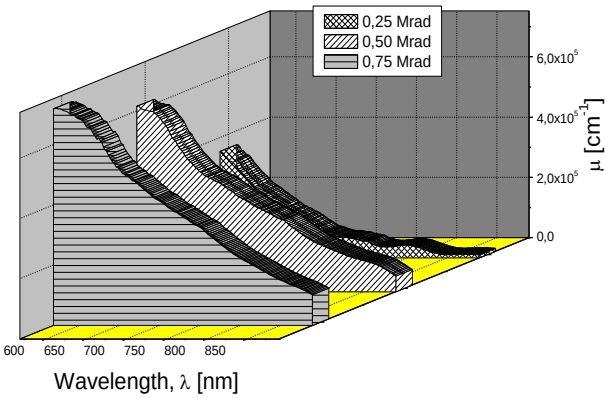

Fig.4 The induced absorption coefficient, μ as a function of wavelength and at different γ-dose.

Fig. 5 shows the spectral variation of the absorption coefficient, α of the AGS films at different γ-dose, as a function of photon energy. A plot of $(\alpha h\nu)^2$ versus $h\nu$ yields a straight lines (Fig. 6a) from which the value of the allowed direct energy gap ($E_{gdir.}$) could be estimated.

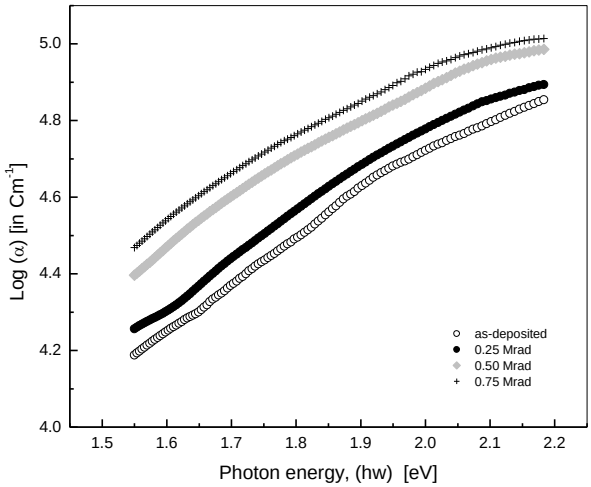

Fig.5 spectral variation of the absorption coefficient at different γ-dose.

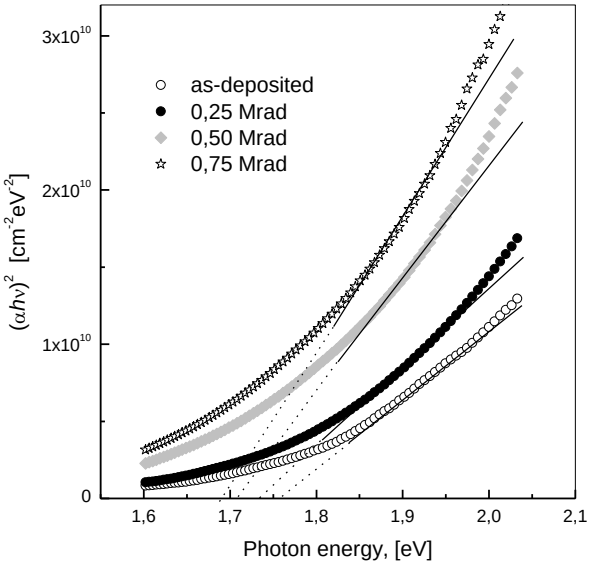

Fig.6a Plots of $(\alpha h\nu)^2$ *vs*. photon energy , $h\nu$.

The calculated optical parameters as a function of g-dose are summarized in Table 1.

Table 1. Optical parameters of $AgGaSe_2$ thin films at different gamma-dose

Sample	E_d	$E_o[eV]$	$n_o(0) = (1+E_d/E_o)^{1/2}$	$\varepsilon = n^2$	$E_g = E_o/2$ [eV]	Band gap	
						$E_g^{direct}[eV]$	$E_g^{ford.}[eV]$
as-deposited	21.416	3.583	2.641	6.977	1.792	1.76	1.904
0.25 Mrad	20.487	3.275	2.693	7.254	1.638	1.72	1.861
0.50 Mrad	19.989	3.146	2.712	7.353	1.573	1.69	1.824
0.75 Mrad	19.542	3.064	2.716	7.378	1.532	1.67	1.785

DISCUSSIONS

Figure (2) illustrates that the films are transparent and exhibits an oscillatory behaviour. The appearance of interference maxima of reflectance spectra (for as-deposited films) at the same wavelength positions of the minima of the transmission spectra indicates the optical homogeneity of the deposited films. A decrease in the transmission spectra and a red shift of the fundamental absorption edge were observed as the irradiation dose increases indicating photodarkening process.

The spectral dependencies of the refractive index and film thickness were calculated from transmission spectra (interference fringes) using Swanepoel method (Swanepoel et al., 1981). It is worth to mention here that a satisfactory agreement between the film thicknesses calculated using Swanepoel method (458.3 nm) and that recorded during evaporation process via quartz crystal thickness monitor (472 nm).

The sets values of refractive index obtained from the application of the above mentioned method were fitted to a reasonable function, such as the two-term Cauchy dispersion relationship, $n(\lambda) = a + b/\lambda^2$ (Swanepoel et al., 1981) It was observed in figure (3) that the refractive index increases with increasing γ-dose, indicating a photo-refraction process. This finding could be the result of interaction of γ-rays with the deposited films causing the creation of electron-hole pairs. This is accompanied by formation of charged metastable states at the chalcogen atom that can react spontaneously with the Ag ions, (depending on the intensity of γ-dose) and probably with different polrizability, i.e. different refractive indices (Salem et al., 2007).

The refractive-index dispersion, $n(\hbar\omega)$, of the investigated samples can be fitted by the Wemple-DiDomenico relationship (Wemple and DiDomenico, 1971):

$$n^2(\hbar\omega) = 1 + \frac{E_d E_o}{E_o^2 - (\hbar\omega)^2}, \qquad 1$$

where E_o and E_d are single-oscillator fitting constants, which measure the oscillator energy and strength, respectively. The oscillator energy, E_o is an `average' energy gap, and it scales with the Tauc gap, $E_g^{opt.}$ i.e., $E_o \approx 2E_g^{opt.}$ as it was found by Tanaka (Tanaka, 1990) and also verified with other amorphous chalcogenide materials. By plotting $(n^2 - 1)^{-1}$ as function of $(\hbar\omega)^2$ and fitting a straight line as shown in the inset of Fig. 3, E_o and E_d can be determined directly from the slope, $(E_o E_d)$ and the intercept on the vertical axis, E_o/E_d, respectively. The calculated values of the dispersion parameters E_o and E_d as well as the refractive index value at $\hbar\omega \to 0$, $n_o^2 = 1 + E_d/E_o$ for the irradiated AGS samples are listed in Table 1.

From the recorded optical transmission before and after exposure the AGS films to γ-dose, a radiation-induced absorption coefficient, μ, defined as,

$$\mu = \frac{1}{d} \ln \frac{T_o}{T}, \qquad 2$$

can be calculated, where *d* is the film thickness, T , T_o are the transmittances before and after irradiation, respectively. It is clear in figure (4) that the induced absorption coefficient increases with the increase γ-dose.

Furthermore, in the fundamental absorption region, the absorption coefficient, α, can be calculated from the transmission spectra using the well-known relation,

$$\alpha = (\frac{1}{t})\ln(\frac{1}{T}) \qquad 3$$

where, t is the film thickness. It was observed in figure (5) that the absorption coefficient for the investigated films have high values (10^4~10^5 cm^{-1}), and was found to increases with the increase in the γ-dose. The analysis of the absorption coefficient in the photon energy range 1.602-2.03 eV was found to follow the relation

$$\alpha = (h\nu)(A/h\nu)(h\nu - E_g)^p \qquad 4$$

with p=1/2 which characterizes an allowed direct optical transition (this transition corresponds to an allowed direct transition from the top of the valence band to the conduction band minimum at the center of the Brillouin zone). The direct energy gap value for the un-irradiated AGS film (1.76 eV) in the present work was found to be in agreement with the previously reported value of 1.8 eV for thermally evaporated AGS films (Shay and Wernic, 1975). While, the analysis of the absorption coefficient in the photon energy range 2.03-2.18 eV, showed that the dependence of the absorption coefficient, α on $h\nu$ could be described by the relation (4), with p=3/2 (Pankove, 1971) (see Fig.6b). This transition corresponds to a forbidden direct transition from the crystal-field-split valence band to the conduction band minimum.

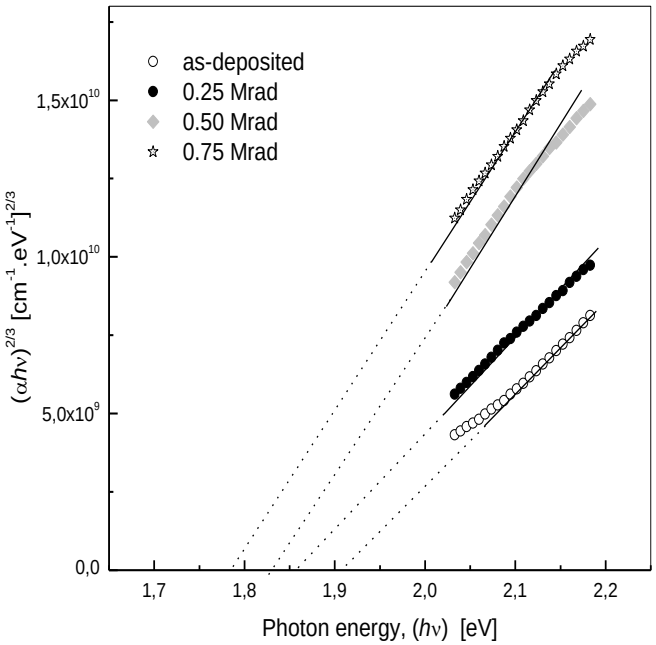

Fig.6b Plots of $(\alpha h\nu)^{2/3}$ *vs*. photon energy, $h\nu$.

CONCLUSIONS

Nearly stoichiometric thin films of $AgGaSe_2$ thin films were deposited, by e-beam evaporation onto clean glass substrates held at room temperature. The effect of γ-dose on the optical transmission spectra of the deposited films was investigated. The absorption edge of the transmission spectra shifted to lower energies as the γ-dose increases, indicating photodarkening process. The refractive index for the investigated films increases with increasing γ-dose indicates a photorefractive process. The γ-dose effect on the refractive index was analyzed according to the well-known Wemple and DiDomenico single-oscillator model. The oscillator energy, E_o, oscillator strength E_d as well as the high frequency dielectric constant, ε_∞ were decreased with increasing γ-dose. The analysis of the optical absorption spectra of the investigated films at different γ-dose revealed the presence of both allowed direct and forbidden direct optical transitions. The energies of such transition have been calculated and were found to decreases with increasing the γ-dose.

REFERENCES

[1] P. J. S. Ewen, A. E. Owen, High Performance Glasses, Blackie, London (1992) 287.

[2] G. Pfeiffer, M. A. Paesler, S. C. Agarwal, J. Non-Cryst. Solids **130**, (1991) 111.

[3] A. M. Andriesh, V.V. Ponomar, V. L. Smirnov, A. V. Mironas, Sov. J. Quantum Electronics **16** (1986) 721.

[4] S. Elliott, "Chalcogenide Glasses", Chapter 7, Mat. Sci. Tech. **9** (1991) 376.

[5] S. Elliott, J. Non-Cryst Solids **81**, (1986) 71.

[6] K. Tanaka, Rev. Solid State Sci. **4** (1990) 641.

[7] K. Shimakawa, A. Kolobov, S.R. Elliott, Advances in Physics **44**, (1995) 475.

[8] M. Frumar, Z. Polak, Z. Cernosek, M. Vlcek, B. Frumarova, Photoinduced Effects in Amorphous Chalcogenides in Physics and Applications of Non-Crystalline Semiconductors in Optoelectronics, Kluwer Academic Publishers (1997), p. 123.

[9] H. Matsuo, K. Yoshino and T. Ikari; Thin Solid Films 515 (2006) 505

[10] P.G. Schunemann, S.D. Setzler and T. M. Pollak; J. Cryst. Growth **211** (2000) 257.

[11] Shay J L and Wernic J H 1975 Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications (Oxford: Pergamon)

[12] Y. S. Murthy, O. Mohammad, Hussain, S. Uthanna, B. S. Naidu and P.J. Reddy; Phys. Lett. A 152 (1991) 311.

[13] Murthy Bhuiyan Soliman Y S, Naidu B S and P.J. Reddy; Mater. Sci. Eng. B (1991)175.

[14] M R A Bhuiyan, M K Rahman and S M Firoz Hasan; J. Phys. D: Appl. Phys. **41** (2008) 235108

[15] H. S. Soliman; J. Phys. D: Appl. Phys. **28** (1995)764.

[16] R. Swanepoel, J. Phys. E 16 (1983) 1214.

[17] A.M. Salem, S.Y. Marzouk, S.H. Moustafa, M.S. Selim; Nuclear Instruments and Methods in Physics Research B 262 (2007) 225.

[18] S.H. Wemple, M. DiDomenico, Phys. Rev. B 3 (1971) 1338.

[19] K. Tanaka, Rev. Solid State Sci. 4 (1990) 641.

[20] J. I. Pankove, Optical Processes in Semiconductors (Prentice-Hall, New York, 1971).