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STUDIES ON THE STRUCTURAL AND OPTICAL PROPERTIES OF $AgIn_{1-X}Ga_XSe_2$ ($0 \le x \le 1.0$) THIN FILMS

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ABSTRACT

Polycrystalline thin films of $AgIn_{1-X}Ga_XSe_2$ (AIGS) with varying x ($0 \le x \le 1.0$) have been grown onto glass substrates by stacked elemental layer (SEL) deposition technique in vacuum (~10^{-6} mbar). The thickness of the films was kept constant at 500 nm measured on line by frequency shift of quartz crystal. The films were annealed in situ at 300°C for 15 minutes. Structural and optical properties of the films were ascertained by X-ray diffraction (XRD) and UV-VIS-NIR spectrophotometry (photon wavelength ranging between 300 and 2500 nm) respectively. The diffractogram indicates that these films are polycrystalline in nature. The optical transmittance spectra reveal a maximum transmission of 85.91% around 1100 nm of wavelength for x = 0.2. A sharp absorption region is evident from the transmittance spectra that indicate a standard semiconducting nature of the films. The abruptness at the fundamental edge is more distinct in the film with x = 0.2. Optical transmittance, reflectance and thickness of the films were utilized to compute the absorption coefficient, band gap energy and refractive index of the films. The optical band gap is found to be direct-allowed. The band gap energy value, found from this study ranging between 2.3 to 2.4 eV, is very close for different gallium content films. The refractive indices increase almost linearly with photon wavelength range between 1300 and 1500 nm.

INTRODUCTION

In recent years, considerable efforts have been made to grow device-quality thin films by optimization of growth parameters for applications in optoelectronic devices. $AgGaSe_2$ is a direct band gap semiconductor that has been studied in many laboratories because of its potential utility in nonlinear frequency converters and photonic devices [1-5]. Our aim is to assess the potentiality of the Stacked Elemental Layer (SEL) deposition method [6-8] to grow the films of desired qualities for photovoltaic applications. For this purpose we have chosen the quaternary compound $AgIn_{1-X}Ga_XSe_2$, where different concentrations of gallium have been added as a dopant. We know that in case of $CuInGaSe_2$ thin film Cu causes shorting effect due to its larger diffusion coefficient. To get rid of this difficulty we replace Cu with Ag and are working in the direction of obtaining a material of desired properties by varying different growth parameters like adding different dopants, varying thickness, annealing temperatures, annealing durations etc. In this paper we present our results for $AgIn_{1-X}Ga_XSe_2$ thin films where we kept the annealing temperature constant at 300°C for 15 minutes and varied x from 0 to 1.

EXPERIMENTAL

Growth of the Films

Three stage thin films of $AgIn_{1-X}Ga_XSe_2$ have been grown onto ultrasonically and chemically cleaned glass substrates by Stacked Elemental Layer (SEL) deposition method in a vacuum of $\sim 10^{-6}$ mbar. An oil diffusion pump (E 306A, Edwards, UK) was used to deposit 500 nm thick films in-situ by thermal evaporation. The rate of deposition was 0.2 nm/sec, 0.3 nm/sec, 0.8 nm/sec and 0.3 nm/sec for Ga, In, Se and Ag, respectively. Thicknesses of individual layers to be deposited were calculated prior to the preparation of the films. During preparation, the thicknesses were measured by frequency shift of quartz crystal which also monitors the rate of deposition. All the films were annealed in-situ at 300°C for 15 minutes.*

Structural Measurements

X-ray diffraction (XRD) method was used to analyze structural property of $AgIn_{1-X}Ga_XSe_2$ thin films. The diffraction patterns were recorded using a Philips PW 3040 X' Pert PRO XRD system with Cu–*Kα* radiation, operated at 40 kV and 30 mA, with angular range $20° \le 2\theta \le 50°$.

Optical Measurements

The dependence of transmittance and specular absolute reflectance of the films as a function of incident photon wavelength were measured using a dual-beam UV-VIS-NIR recording spectrophotometer (Shimadzu, UV-3100, Japan) in the photon wavelength range between 300 and 2500 nm. Light signals coming from the samples were detected by an integrating sphere. The spectrophotometer was used to measure the total thickness of the film by infrared interference method [9] to confirm the thickness measured by frequency shift of quartz crystal during the preparation of the films. The thickness of a film given by this method is

$$d = \frac{\Delta m}{2\sqrt{n_1^{\,2} - \sin^2\theta}} \frac{1}{(1/\lambda_1) - (1/\lambda_2)}$$

where, n_1 and n_2 are the refractive indices of the glass substrate and film respectively. θ is the incident angle of light to the sample. λ_1 and λ_2 are the peak or valley wavelengths in the reflectance spectrum and Δm is the number of peaks or valleys between λ_1 and λ_2, where $\lambda_2 > \lambda_1$.

If *T* represents the transmittance at normal incidence and *R* is the reflectance at near-normal incidence of light on the films, then the expression for the multiple reflected

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* *Note: More than one growth parameter can not be changed simultaneously. Here x (i.e., composition) has been varied keeping annealing temperature and time constant at 300°C and 15 min, respectively.*

system is given by Heavens [10]. Tolmin's [11] simplified expression for absorbing films on non-absorbing substrates which is given by

$$\frac{1-R}{T} = \frac{1}{2n_2(n_1^2+k_1^2)} \times \left[n_1 \left\{ \left(n_1^2 + n_2^2 + k_1^2 \right) \sinh 2\alpha_1 + 2n_1 n_2 \cosh 2\alpha_1 \right\} \right.$$
$$\left. + k_1 \left\{ \left(\left(n_1^2 - n_2^2 + k_1^2 \right) \sin 2\gamma_1 + 2n_2 k_1 \cos 2\gamma_1 \right) \right\} \right]$$

where, n_1 and n_2 are the refractive indices of the film and substrate respectively. k_1 is the extinction coefficient of the film. $\alpha_1 = 2\pi k_1 d / \lambda$, $\gamma_1 = 2\pi n_1 d / \lambda$, where d is the thickness of the film and λ is the wavelength of light. This equation has been solved by a computerized iteration process for k_1 taking n_1 = 2.7, which is the average of $AgGaSe_2$ and $AgInSe_2$ thin films. For this iteration process n_2 was taken as 1.45. Absorption coefficient α was calculated using the relation $\alpha = 4\pi k_1 / \lambda$.

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction (XRD) pattern of $AgIn_{0.8}Ga_{0.2}Se_2$ thin film of 1000 nm thickness.

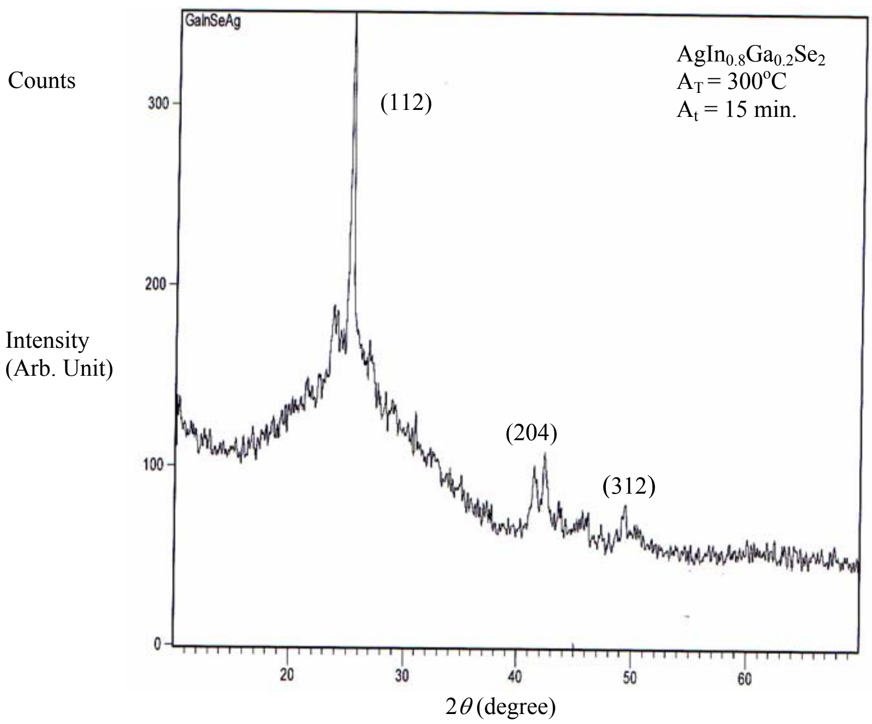

Fig. 1. The x-ray diffraction pattern of $AgIn_{0.8}Ga_{0.2}Se_2$ thin film.

The diffractogram reveals that the films are polycrystalline with a tetragonal structure and the preferred orientation is (112).

The optical transmittance spectra having various gallium concentrations are shown in Figure 2. The transmittance reaches a maximum value at different photon wavelengths for different gallium concentrations. The transmittance is maximum for x = 0.2 and reaches a value of 85.91% at 1100 nm of photon wavelength. The transmittance peak is sharper for this sample. After 1100 nm the transmittance reduces drastically and falls to almost zero at around 300 nm.

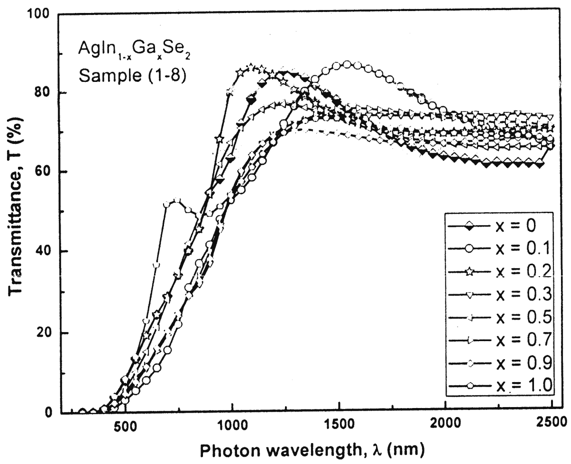

Fig. 2. Dependence of optical transmittance on photon wavelength for $AgIn_{1-x}Ga_xSe_2$ thin films having different Ga contents.

The absorption coefficient, α as a function of photon energy is plotted in Figure 3. The Figure shows clear steeper absorption regions for x = 0, 0.1 and 0.2. No significant absorption region is observed for samples with other gallium content films.

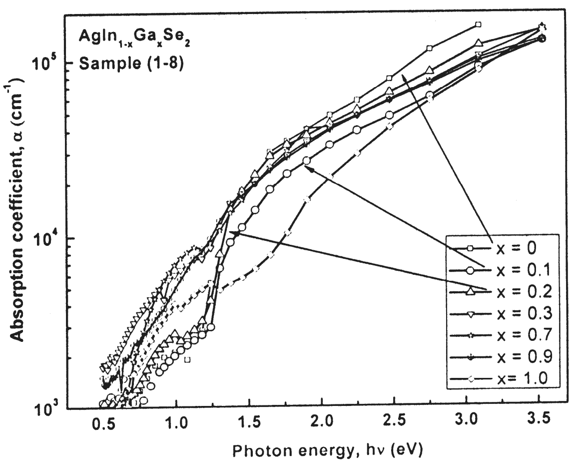

Fig. 3. Dependence of absorption coefficient on photon energy for $AgIn_{1-x}Ga_xSe_2$ thin films having different Ga contents.

The figure also demonstrates clearly that the absorption region is the steepest for the film with x = 0.2. This is an indication that this sample possesses better optical property than any other x-varying films. The absorption coefficients, α above the fundamental edge have values higher than 10^5 cm^{-1}. The rise of α in the photon energy range 1.1 eV to 1.3 eV follows a relation for an allowed direct interband transition [12], described by

$$\alpha = \frac{A}{h\nu}\left[h\nu - E_g\right]^{1/2}$$

where E_g is the gap energy of the interband transition and A is a parameter that depends on the probability of transition and the refractive index of the material.

The band gap energies E_g and the value of A (Table 1) were extracted from the plot of $(\alpha h\nu)^2$ versus $h\nu$ in the range $2.48 \leq h\nu \leq 3.54$ eV as shown in Figure 4.

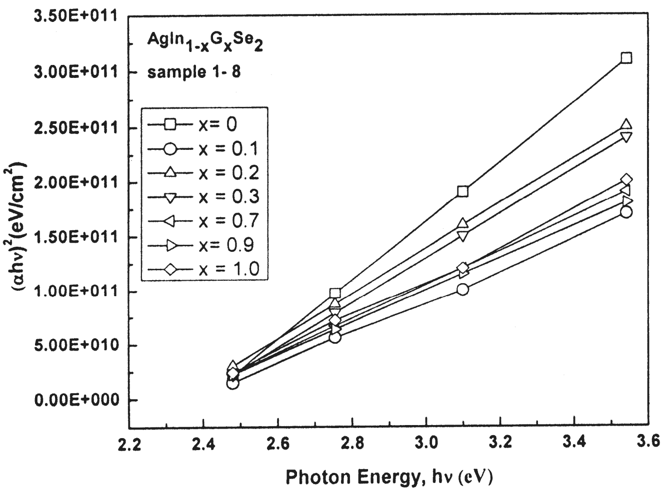

Fig. 4. Variation of $(\alpha h\nu)^2$ with photon energy for $AgIn_{1-x}Ga_xSe_2$ thin films.

Extrapolation of the linear part of this plot intercepts to the x-axis and gives the value of band gap energies, E_g (Table 1).

Table 1.
Optical parameters of $AGIN_{1-X}GA_XSE_2$ thin films.

Sample	x	Energy gap, E_g (eV)	A (cm^{-1} $eV^{1/2}$)
1	0	2.4	5.2×10^5
2	0.1	2.38	3.8×10^5
3	0.2	2.34	4.6×10^5
4	0.3	2.3	4.5×10^5
5	0.7	2.33	3.99×10^5
6	0.9	2.33	3.87×10^5
7	1.0	2.31	4.18×10^5

The value of E_g is 2.31 eV for $AgGaSe_2$ in our case which is similar as obtained by Hsu-Cheng Hsu et al. [1] for single crystals of $AgGaSe_2$. The values of energy gap show no noticeable correlation with x-variation.

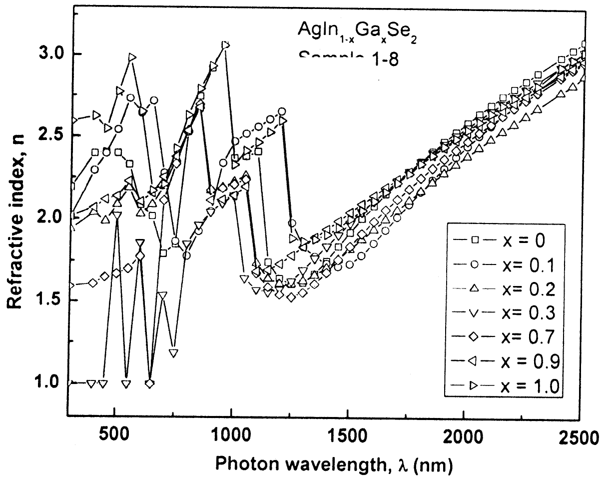

Fig. 5. Dependence of refractive index on photon wavelength of $AgIn_{1-x}Ga_xSe_2$ thin films with different Ga concentrations.

Dependence of refractive index on photon wavelength of $AgIn_{1-x}Ga_xSe_2$ thin films with different Ga concentrations is shown in figure 5. It is evident that the refractive index increases linearly with photon wavelength in the range between 1500 to 2500 nm.

CONCLUSIONS

The nature of band gap energy of $AgIn_{1-X}Ga_XSe_2$ ($0 \leq x \leq 1.0$) is direct allowed. Sharp absorption regions are found for films with x = 0, 0.1 and 0.2. Above x = 0.2 the film quality decreases. Even the absorption region is not prominent for the samples with x > 0.2. The band gap energy varies from 2.30 to 2.40 eV that has no systematic correlation with different Ga contents in $AgIn_{1-x}Ga_xSe_2$ films. Refractive index increases linearly with photon wavelength in the range between 1500 to 2500 nm. On the basis of abruptness of absorption characteristics and the nature of x-ray diffraction, it may reasonably be concluded that maximum limit of Ga inclusion in $AgIn_{1-X}Ga_XSe_2$ is 20% to get good-quality films. Films with 20% Ga-content give the best optical characteristics.

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