

OPTICAL PROPERTIES OF LOW RESISTIVE SILVER DOPED ZINC SELENIDE ROUGH FILMS

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Closed space sublimation (CSS) method was used to deposit ZnSe films on glass substrate. Post silver doping of the films was achieved by ion exchange process. Considerable reduce of electrical conductivity accompany with decrease of optical transmission as silver concentration, in the films, increases. The optical properties, thickness and roughness of the films were determined by fitting the optical transmission as function of wavelength in UV-VIS-NIR range. The effect of surface roughness, on transmittance spectra, was introduced in transmittance formula which used for fitting the transmittance data. The fitting involve using appropriate model for refractive index, as well as absorption coefficient, as a function of wavelength. X-ray diffraction of the films were also recorded to reveal the structure of the films. The elemental composition of the films were found by energy dispersive system (EDS).

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1. Introduction

ZnSe as II-VI semiconductor material, with direct band gap ~ 2.7 eV, is a promising material for different optoelectronic applications [1-13]. In addition, it may use as window layer for CdTe based solar cells [2,4,5]. A number of techniques have been utilized to deposit ZnSe films such as thermal evaporation [13,14], electro-deposition [3,4], chemical path deposition [5,10], spray pyrolysis [6,7], co-evaporation [8,9] and closed space sublimation [11,12]. Silver, as group I element, could be use as substitution acceptor dopant, in II-VI materials [8,15,16], in order to alter the electrical conductivity of the group II-VI semiconductors.

This paper report the deposition ZnSe films by energy effective CSS method and the effect of silver doping on optical properties of the films. The structure and DC electrical conductivity also reported.

2. Experimental procedure

Pure zinc selenide material (99.99%), in form of grain powder, was used to deposit the films on cleaned transparent glass substrate. The details of the experimental setup, for CSS method, are given in reference [16]. The source material and substrate temperatures were kept at 780 °C and 480 °C respectively. The deposition take place under pressure of 0.01 mb. The source material and the substrate were 1.0 cm apart and the deposition time was fixed for all films.

The pre-prepared films were immersed in silver nitrate solution, at 60 °C, with concentration of 0.5g per liter. The immersion time varies from 30 to 300 seconds as in table 1. The next step was rinsing the films with distilled water and dry it. Further the immersed films were heat treated in vacuum, at 400 °C, for one hour to ensure the diffusion of Ag into the entire film [8]. The films compositions were obtained by energy dispersive system (EDS), while the structure were studied by x-ray diffraction. The dark DC conductivity, was measured at room temperature

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using Van der Pauw method. The optical transmission, in range of 400 to 2000 nm, were recorded with the help of UV-VIS-NIR spectrophotometer.

2. Theoretical background

The transmittance formula, where the reflection from the second interface of the substrate and the effect of finite substrate are included, is given as [17]:

$$T = \frac{(1 - \rho)T_{123}U}{1 - \rho R_{321}U^2} \quad (1)$$

$$R_{321} = r_{321}r_{321}^* \quad (2)$$

$$T_{123} = (n_2 / n_1)t_{123}t_{123}^* \quad (3)$$

$$t_{123} = \frac{t_{12}t_{23}\exp(i\psi/2)}{1 - r_{21}r_{23}\exp(i\psi)} \quad (4)$$

$$r_{321} = \frac{r_{32} + r_{21}\exp(i\psi)}{1 + r_{32}r_{21}\exp(i\psi)} \quad (5)$$

where t_{123} and r_{321} are the amplitude of the electric field of the wave reflected and transmitted in 321 and 123 directions respectively.

$$r_{ij} = \frac{N_i - N_j}{N_i + N_j}, \quad t_{ij} = \frac{2N_i}{N_i + N_j} \quad (6)$$

$$N_i = n_i + ik_i$$

Here n_i and k_i is the real part and the imaginary part (extinction coefficient) of the complex refractive index in air (region 1), film (region 2) and substrate (region 3). The parameters r_{ij} and t_{ij} are the Fresnel coefficient of reflected and transmitted wave in different regions and ψ is the phase difference of the wave between two interfaces.

$$\psi = 4\pi N_2 d / \lambda = 4\pi n_2 d / \lambda + 4\pi k_2 d / \lambda = \phi + i\alpha d$$

where λ is the wavelength, d is the film thickness, ϕ is the phase angle and α is the absorption coefficient. The modified Fresnel coefficient of reflected and transmitted waves at rough surface [18], where the r.m.s. height of surface irregularity $\sigma \ll \lambda$, are:

$$r'_{21} = r_{21} \exp[-2(2\pi\sigma/\lambda)^2 n_2^2] = \beta r_{12} \quad (7)$$

$$t'_{12} = t_{12} \exp[-\frac{1}{2}(2\pi\sigma/\lambda)^2 (n_1 - n_2)^2] = \gamma t_{12} \quad (8)$$

Substitution equations (7) and (8) into Equation (1) gives:

$$T = \frac{A \exp(\alpha d)}{B \exp(2\alpha d) + C \exp(\alpha d) + D} \quad (9)$$

where the parameters A, B, C, D, U and ρ are given as:

$$A = \gamma^2 [16n_1 n_3 (1 - \rho)(n_2^2 + k_2^2)U], \quad B = st - \rho s v U^2,$$

$$C = \beta \{ [2(4n_3 k_2^2 - ZY) \cos \phi + 4k_2 (n_3 Y + Z) \sin \phi] - \rho U^2 [4k_2 (Z - n_3 Y) \sin \phi - 2(ZY + 4n_3 k_2^2) \cos \phi] \}$$

$$D = \beta^2 [uv - \rho t u U^2],$$

$$u = (n_1 - n_2)^2 + k_2^2, \quad v = (n_2 - n_3)^2 + k_2^2, \quad s = (n_1 + n_2)^2 + k_2^2,$$

$$t = (n_2 + n_3)^2 + k_2^2, \quad Y = n_2^2 - n_1^2 + k_2^2, \quad Z = n_2^2 - n_3^2 + k_2^2,$$

$$\rho = [(n_1 - n_3) + k_3^2] / [(n_1 + n_3) + k_3^2], \quad n_3 = n_1 [1/T_s + (1/T_s - 1)^{1/2}],$$

$$U^{-1} = \frac{(1 - \rho)^2}{2T_s} + \left[\frac{(1 - \rho)^4}{4T_s^2} + \rho^2 \right]^{1/2},$$

where T_s is the transmission of the substrate and, for transparent substrate $U=1$ and $k_3=0$. In case of transparent substrate $k_3=0$ then $U=1$, $n_1=1$ and $k_2^2 \ll n_2^2$ in weak and medium absorption region. Equation 9 can be rewritten as

$$T = \frac{Ax}{B - Cx \cos(\phi) + Dx^2} \quad (10)$$

$$A = 16 \gamma^2 n_3 n_2^2, \quad B = (n_2 + 1)^3 (n_2 + n_3^2), \quad C = 2 (n_2^2 - 1) (n_2^2 - n_3^2) \beta$$

$$D = (n_2 - 1)^3 (n_2 - n_3^2) \beta^2, \quad \phi = 4\pi n_2 d / \lambda, \quad x = e^{-\alpha d}.$$

The refractive index, of the substrate, $n_3 = 1/T_s + (1/T_s^2 - 1)^{1/2}$, where T_s is the transmission of the substrate. Here, the refractive index of the films obey the simple classical dispersion relation for a single oscillator centered at wavelength λ_0 [15,19] is expressed by

$$n_2 = \left(1 + \frac{(n_0^2 - 1)\lambda^2}{\lambda^2 - \lambda_0^2} \right)^{1/2},$$

where n_0 is the infinite wavelength refractive index. The wavelength dependence of the absorption process is complicated, resulting from impurity, defects or multi-phonon absorption [20], therefore, in case of low absorption coefficient α , it may be expanded in a Taylor series around the photon energy far from absorption line. If only terms up to second degree are included (α varies slowly with λ), the relation for α can be written as: $\alpha = c + g/\lambda + f/\lambda^2$, where c , g and f are fitting parameters. The values of σ , d and n_2 obtained by fitting of transmittance data, in transparent region, to equation 11. Furthermore these parameters were used to calculation α in the high absorption region (below 500 nm). The exact solution of equation 10 for x is:

$$x = \{ (C \cos(\phi) + A/T) - [(C \cos(\phi) + A/T)^2 - 4BD]^{1/2} \} / (2D) \quad (11)$$

For allowed transition, α varies with photon energy ($h\nu$) as the well-known dependence $\alpha \sim (h\nu - E_g)^{1/2}$. Near the absorption edge, the optical energy gap (E_g) is obtained by extrapolating $(\alpha)^2$ against photon energy plot

4. Results and discussions

The composition of the films, are shown in Fig.1, clearly shows the increase of Ag concentration along with decrease of Zn concentration as the immersion time increased. This indicates the replacement of Zn elements by Ag. However the speed of ion exchange process slow down as immersion time increased, which is common in case of ion exchange process [9] as the films surface gradually covered by Ag layer reducing the quantity of zinc in which exposed to the surface.

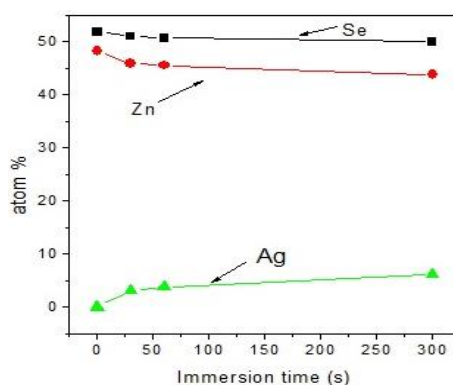


Fig.1. Elemental concentration of Se, Zn and Ag in the films.

The Ag concentration, for the film immersed for 300 second, was $\sim 6\%$ which much higher than that reported for films prepared by thermal evaporation [9]. One can guess that the more roughness, of the film surface, the higher of the speed of the ion exchange process due to larger surface expose to the solution. Due to that it's important to study the thickness roughness of the films. The x-ray diffraction pattern (Figure 2.) reveal the cubic zinc blend structure of the films with (111) direction as well defined preferred orientation of the films, indicating good crystalline of the films as the films were deposited at, comparatively, high substrate temperature.

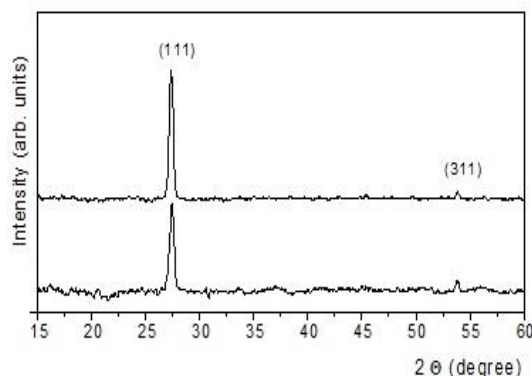


Fig. 2. X-ray diffraction pattern of as deposited film (up) and immersed, for 300s, (down).

The DC electrical resistivity was credibly reduced from $\sim 10^7 \Omega\text{-cm}$ for as deposited films to $\sim 10^3 \Omega\text{-cm}$ and the films conductivity type was altered from n-type (for as deposited film) to p-type.

After immersion, in silver nitrate solution, the color of the film converted from yellowish to grayish yellow. This accompanied with decrease of the films transmittance as shown in Fig. 3.

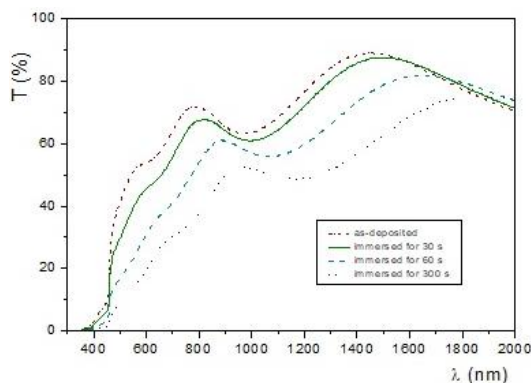


Fig. 3. Transmittance curves of all the films.

The thickness, surface roughness and refractive index, as a function of wavelength, of each film were obtained by fitting of the transmittance data to equation 10. Fig.4 shows the fitting of as deposited film and other film immersed for 60 s . It is obvious that the fitting curve has excellent match with the experimental data. Further, the absorption coefficient, near the absorption edge, was calculated by equation 11, using the values of thickness, roughness and refractive index deduced from fitting of the transmittance curve.

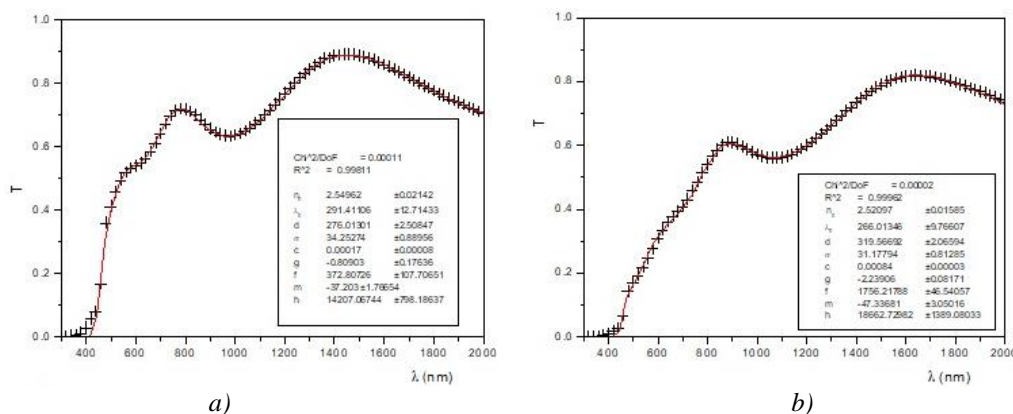


Fig. 4. Fitted transmittance data for as deposited film (a) and immersed, for 60s, b).

The optical energy gap was found by plotting of the square of absorption coefficient versus the photon energy, using the known relation for direct band gap semiconductors $\alpha \sim (h\nu - E_g)^{1/2}$ and by plotting graph between square of absorption coefficient versus photon energy and extrapolation the liner region to photon energy axis (Fig.5).

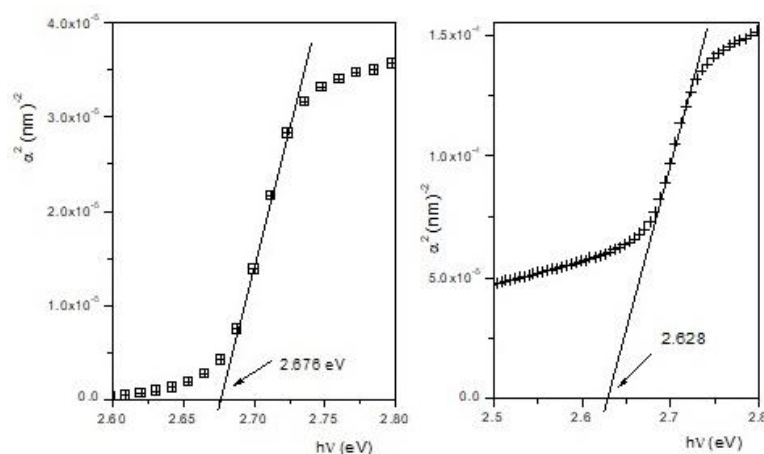


Fig. 5. Square of absorption coefficient versus photon energy for as deposited film (left) and immersed, for 300s, (right).

The results, of optical calculations, are given in table 1. This results shows minute change of surface roughness is due ion exchange process, which indicates that deposition parameters have more critical influence than post treating, which in agree with results reported earlier using atomic force microscopy [17].

Table1. Thickness, surface roughness, refractive index an optical energy gap of the films.

Immersion time (s)	Thickness (nm)	Surface roughness (nm)	Refractive index (Eq. 2)		Optical energy gap (eV)
			n_0	λ_0	
0	276	34.2	2.55	291	2.676
30	287	33.1	2.53	292	2.668
60	320	31.2	2.52	266	2.656
300	334	31.4	2.68	193	2.628

Observable decreasing of optical band gap associated with significant improve of electrical conductivity along with small change of refractive index points toward high doping occurs in the material.

5. Conclusions

Using a transmittance formula that including the surface roughness, of the films, allows us to utilize the transmittance spectra to determine the optical properties, of rough films, with good precision. The results show that no critical change in the surface roughness, of ZnSe films, due to post immersion in silver nitrate. The reducing of transmittance is due to increase of the films absorption, as the silver impurity was increased in the films. Observable narrowing of the band gap was occur due to high doping in the films as the immersion time was increased.

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