

# Optical and structural properties of silver doped ZnSe thin films prepared by CSS and ion exchange process

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## ABSTRACT

ZnSe thin films were prepared by, simple low cost, closed space sublimation method (CSS). The silver doping was achieved by ion exchange process, i.e. immersing the films in low concentrated silver nitrate solution for different time periods and flowed by heated treatment in vacuum. The effect of silver concentration on the optical properties, such as refractive index, absorption coefficient and optical band gap, have been calculated from the normal transmission spectra in UV, Visible and NIR region. The structure of the films was studied by X-ray diffraction. The EDS attached to SEM was used to determine the composition of the films. The electrical resistivity, at room temperature, was also measured and it was reduced considerably as silver concentration increased.

Keywords : Thin films, ZnSe, Ag, transmittance, XRD, EDX.

## 1. INTRODUCTION

ZnSe is an II-VI compound semiconductor, mainly used for wide variety of applications in opto-electronic devices. It is well known as high refractive index material and infrared antireflection coating for solar cells. ZnSe, as a wide band-gap (~2.7 eV) compound semiconductor with cubic zinc blend structure, is found to be very promising material for opto-electronics and hetero-junction solar cells<sup>1-15</sup>. A broad variety of techniques has been used for the deposition of ZnSe films such as, atomic layer deposition<sup>1</sup>, thermal evaporation<sup>2-6</sup>, chemical bath deposition<sup>7-9</sup>, electro-deposition<sup>10</sup>, pulsed laser deposition<sup>11</sup>, brush plated<sup>12</sup>, spray pyrolysis<sup>13</sup>, molecular beam deposition<sup>14</sup> and closed space sublimation<sup>15</sup>. And it was reported that electrical, structural and optical properties of the films are sensitive to deposition conditions. Furthermore silver as group I element acts as acceptor donor for II-VI compound semiconductors<sup>16,17</sup>, which leads to improve the electrical conductivity. In the other hand ion-exchange process was, recently, successfully used for doping II-VI semiconductor films with silver and copper<sup>16, 18-23</sup>.

In this work we deposited ZnSe films with CSS (closed space sublimation) method. This method is simple, low cost and widely used for II-VI semiconductor films. Ion exchange process, by immersing the films in diluted AgNO<sub>3</sub> solution, was used for doping the films with Ag. In this regard the electrical conductivity of the films was studied as a function of immersion time, of the films in AgNO<sub>3</sub> solution. Furthermore the optical, such as refractive index, absorption, surface roughness and the optical energy gap, and structural properties of the films were also studied. This is due to the importance, of these properties, in the application of the ZnSe films.

## 2. EXPERIMENTAL METHODS

High purity (99.99%) ZnSe grains were used as a source material for the films deposition on extra-white glass substrates (2.5cm × 5cm). Before deposition, the substrate was cleaned by diluted H<sub>2</sub>SO<sub>4</sub> solution, then rinsed by distilled water and I. P.A(isopropyl alcohol) and then dried by dry nitrogen gas. Source material was put in the graphite boat, to be heated by 1000W quartz lamp. The source and substrate heaters ( quartz lamps) were connected to the main through two separate triacs. The gates of the triacs were connected to temperature controllers. The, k-type, thermocouples of the temperature controllers were inserted into the source graphite boat and the graphite substrate supporter. The CSS system,

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used in our experiment, is shown in figure 1. Substrate was fixed at a distance of about 10 mm from the source material. The chamber was closed and evacuated, by the help of rotary pump, to  $\sim 0.01$  mbar. The substrate and source temperatures were kept at  $480^\circ\text{C}$  and  $780^\circ\text{C}$ , respectively. The chamber was evacuated for 30 minutes before starting the source and substrate heating. After deposition, the source heater was turned off, while the substrate remains at the deposition temperature for 30 minutes. This was to allow the source temperature to cool down, avoiding further deposition at lower substrate temperature. The film remains under vacuum till the source temperature reduced to below  $100^\circ\text{C}$ , to avoid the oxidation of the film.

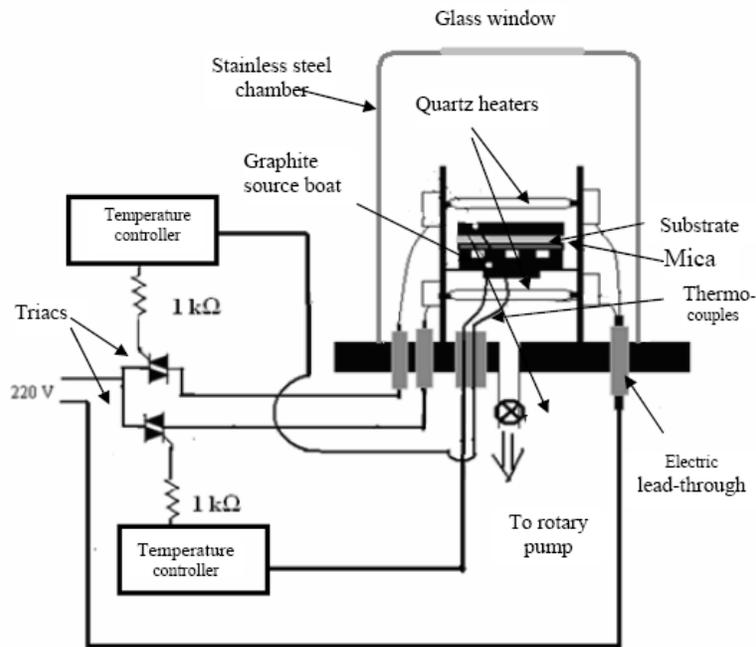


Fig. 1. Block diagram of coating unit, in which used for CSS method .

Numbers of films were prepared with similar deposition parameters to study the effect of post treating in  $\text{AgNO}_3$  solution. The solution contained 0.5g of  $\text{AgNO}_3$  in 1 liter of distilled water. The solution was kept at  $60 \pm 2^\circ\text{C}$ . The films were immersed for different time, as listed in table 1. After immersion, the films were cleaned in distilled water and dried by nitrogen gas. Next step was heating the immersed films, in vacuum of  $\sim 10^{-2}$  mbar, at  $400^\circ\text{C}$  for 1 hour to ensure the diffusion of Ag into the entire film<sup>6</sup>. Ion exchange process occurs on the films surface, i.e. Ag layer formed above the ZnSe film. So heating the films, at high temperature, cause diffusion of Ag atoms in the entire film. Further, studying the Ag doped ZnSe films not the properties of Ag layer on the surface of ZnSe film.

X-ray diffraction (XRD) patterns, using  $\text{Cu-K}_\alpha$  radiation, were used to study the structure of the films. The optical transmission spectra in the range 300-2000 nm were recorded by Perkin-Elmer, Lambda19, UV-VIS-NIR spectrophotometer with UV-WinLab software. The dark electrical DC conductivity, of square cut pieces of the films with evaporated Au contact, according to Van der Pauw geometry, was measured at room temperature using four contact, Van der Pauw, method. The compositions of the films were detected using energy dispersive system (EDS) attached to scanning electron microscope.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Compositions and structure

The EDS spectra of film IV, immersed film for five minutes in  $\text{AgNO}_3$  solution, are shown in Figure 2. The compositions results are listed in table 1. The ratio of Se is higher than Zn in As-deposited films by  $\sim 2\%$ . This is within the expected error of EDX method. However the ratio of Zn to Se in ZnSe film may change as deposition parameters changes<sup>5</sup>. The results also show decreasing in the Zn concentration accompany with increasing in Ag concentration as the immersion time, of the films in  $\text{AgNO}_3$  solution, increases. The results also show that the silver concentration does not increase linearly with immersion time. It can be explained by the fact that an ion process take place at the film surface, which expose to the solution. So the exchange of Ag ions with ZnSe has been decreased when the film surface was covered with few layers of Ag. The observed Ag peaks in the EDS spectra are taken from the area analysis of the thin films which shows that EDS is more powerful technique, than XRD to detect the concentration of the dopant in the thin films. One peak related to silicon appears in EDX spectra as a contribution from the glass substrate, science the film thickness below 500 nm.

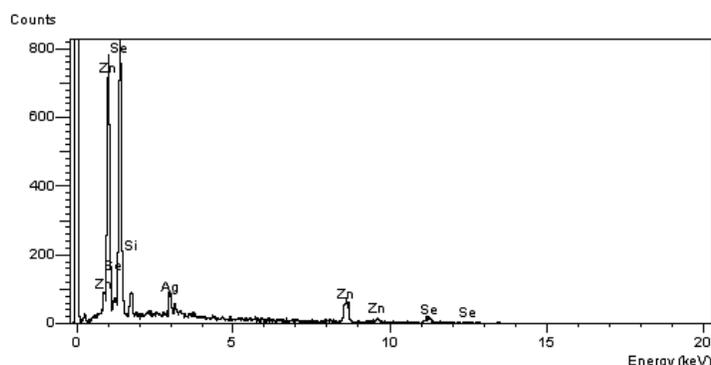


Figure 2 EDS spectra of film IV.

ZnSe can exist in a cubic as well as a hexagonal crystalline phase. X-ray diffraction patterns of the films are shown in figure3. Three peaks are observed that correspond to cubic ZnSe (111), (221) and (311) reflections. All film are cubic in structure and the preferred orientation is [111] direction. The intensities of (111) peak related to immersed films are lower than the intensity of (111) peak in as deposited film. The cubic structure, with (111) orientation, is the most common structure for ZnSe films deposited with different methods<sup>2-6, 8, 12, 13, 15</sup>, while (220) preferred orientation was reported in case of electro-deposition of ZnSe films<sup>10</sup>. Estimated average crystallite size, using Scherrer's formula<sup>3,4</sup>, is  $\sim 25$  nm. The crystalline size is not depending on the immersion in  $\text{AgNO}_3$  solution. This may be due that the deposition conditions, which have more effect on the structure, are the same for all films. No peak corresponds to Ag, or Ag compounds, are detected. This may be attributed to the minute quantity of Ag in the films, which below the detection limit of XRD.

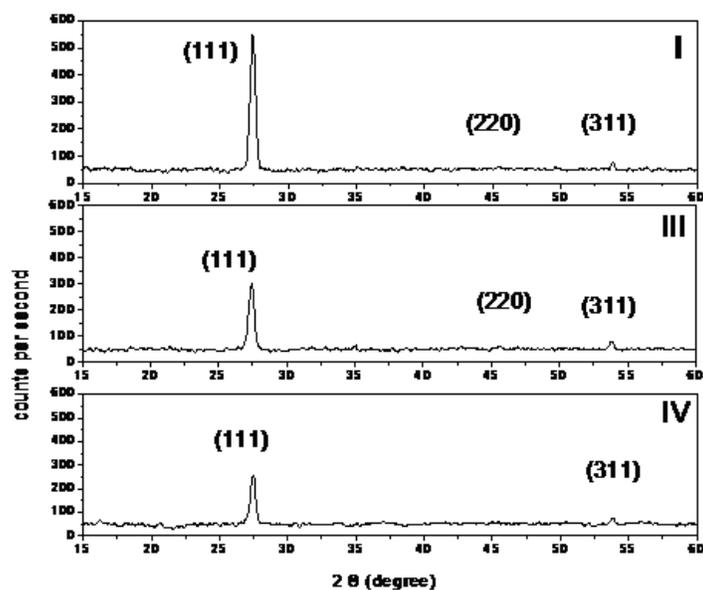
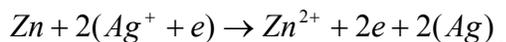


Figure 3. XRD pattern of as deposited film ( I) and immersed films (III and IV).

Due to an ion exchange in  $\text{AgNO}_3$  solution different ways of Ag incorporation into ZnSe may be possible. For example, by substitution of  $\text{Zn}^{2+}$  by  $\text{Ag}^+$  the following reaction is possible<sup>6</sup>,



Alternatively, Ag might be incorporated interstitially in ZnSe. Although the X-ray diffraction pattern did not show any peaks corresponding to Ag or  $\text{Ag}_2\text{Se}$ . Nevertheless the EDS results ensure the presence of Ag.

### 3.2 Electrical resistivity

The DC electrical resistivities of the films are listed in table 1. The resistivity is significantly decreasing as the Ag concentration increases. The P-type conductivity of the immersed films was verified by well known hot probe method. The conductivity and EDX results, i.e. increasing of Ag concentration accompany with decreasing of Zn concentration, lead us to judge that substitution of Zn by Ag ions was the most dominant process, in which occurs due to immersing the films in  $\text{AgNO}_3$  solution followed by heated treatment in vacuum.

Table 1. Immersion time, compositions and DC electrical resistivity of different films.

Film number	Immersion time (s)	Elemental concentration (Atom. %)			Resistivity ( $\Omega\text{-cm}$ )
		Zn	Se	Ag	
I (as-dep.)	0	48.2	51.8	0	1.7 E7
II	30	45.9	51.0	3.1	1.9 E4
III	60	45.5	50.7	3.8	5.1 E3
IV	300	43.8	50.1	6.1	7.5 E2

### 3.3 Optical analysis

The As-deposited films were transparent and yellowish color. However the films color was changed to yellowish gray color after immersion in  $\text{AgNO}_3$  solution. Figure 4 shows the transmittance spectra of the as-deposited film in addition to the other films. It is clear that the film prepared at this substrate temperature is transparent in the visible and near infrared (NIR) ranges of the optical spectra. The transmittance immersed films decreases as the Ag increases.

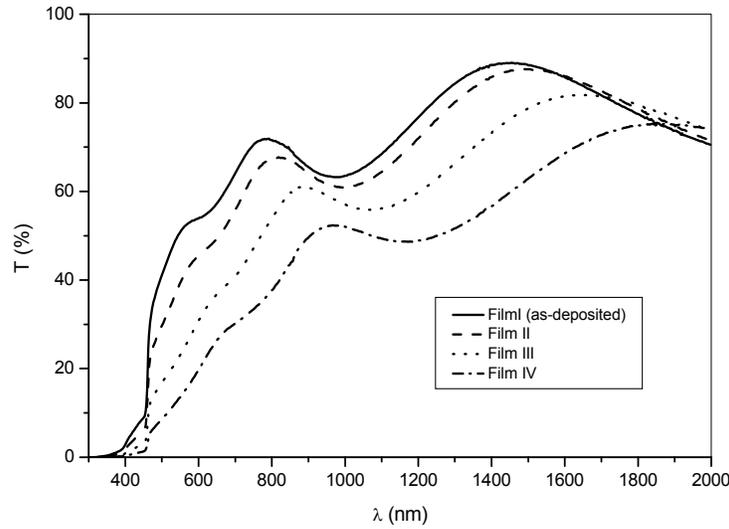


Figure films4. Transmittance of as-deposited and immersed.

The film thickness and the optical properties such as, refractive index, absorption coefficient, and optical band gap are calculated from the transmission spectra. Due to the effect of surface roughness on the optical transmission of the films, transmission formula<sup>17</sup>, which includes the roughness, is used as

$$T = \frac{A_1 \exp(\alpha d)}{B_1 \exp(2\alpha d) + C_1 \exp(\alpha d) + D_1} \times \frac{B_2 \exp(2\alpha d) + C_2 \exp(\alpha d) + D_2}{B_2 \exp(2\alpha d) + C_3 \exp(\alpha d) + D_3} \quad (1)$$

$$A_1 = \gamma^2 [16n_1 n_3 (1 - \rho)(n_2^2 + k_2^2)U], \quad B_1 = st - \rho sv U^2, \quad B_2 = st$$

$$C_1 = \beta \{ [2(4n_3 k_2^2 - ZY) \cos \phi + 4k_2 (n_3 Y + Z) \sin \phi] - \rho U^2 [4k_2 (Z - n_3 Y) \sin \phi - 2(ZY + 4n_3 k_2^2) \cos \phi] \}$$

$$C_2 = \eta \{ 2(4n_3 k_2^2 - ZY) \cos \phi + 4k_2 (n_3 Y + Z) \sin \phi \}, \quad C_3 = \beta \{ 2(4n_3 k_2^2 - ZY) \cos \phi + 4k_2 (n_3 Y + Z) \sin \phi \}$$

$$D_1 = \beta^2 [uv - \rho tu U^2], \quad D_2 = \eta^2 [uv], \quad D_3 = \beta^2 [uv], \quad u = (n_1 - n_2)^2 + k_2^2, \quad v = (n_2 - n_3)^2 + k_2^2,$$

$$\eta = \exp[-2(2\pi\sigma/\lambda)^2 n_1^2], \quad \beta = \exp[-2(2\pi\sigma/\lambda)^2 n_2^2], \quad \gamma = \exp[-\frac{1}{2}(2\pi\sigma/\lambda)^2 (n_1 - n_2)^2].$$

$$D_1 = \beta^2 [uv - \rho tu U^2], \quad D_2 = \eta^2 [uv], \quad D_3 = \beta^2 [uv], \quad u = (n_1 - n_2)^2 + k_2^2, \quad v = (n_2 - n_3)^2 + k_2^2,$$

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

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

$$U^{-1} = \frac{(1 - \rho)^2}{2T_s} + \left[ \frac{(1 - \rho)^4}{4T_s^2} + \rho^2 \right]^{1/2}, \quad \alpha = 4\pi k_2 / \lambda, \quad \phi = 4\pi n_2 d / \lambda,$$

where  $n_i$  is the real part and  $k_i$  is the imaginary part (extinction coefficient) of the complex refractive index of air ( $n_1, k_1$ ), film ( $n_2, k_2$ ) and substrate ( $n_3, k_3$ ),  $d$  is the film thickness,  $\lambda$  is the wavelength,  $\alpha$  is the absorption coefficient,  $\sigma$  is the rms (root mean square) height of surface irregularity (roughness) and  $T_s$  is the transmittance of the substrate. Equation (1) was used for fitting the transmittance spectra, in order to evaluate  $n, d, \sigma$  and  $\alpha$ .

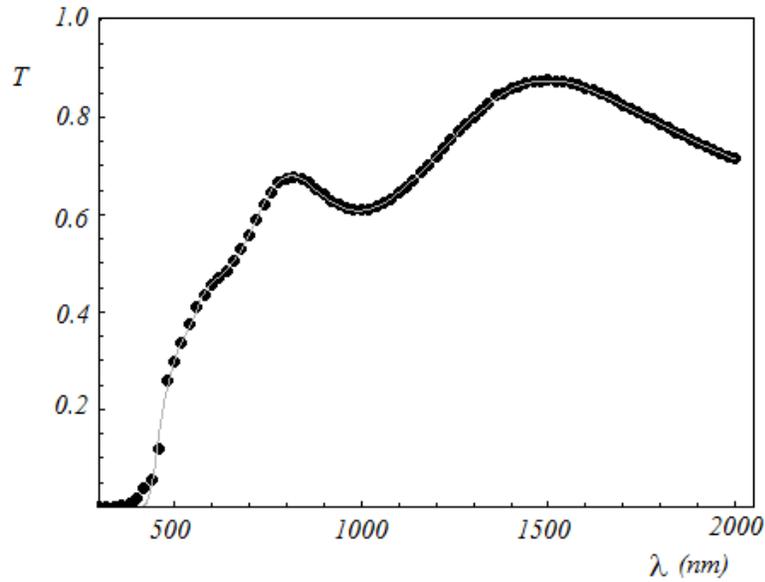


Figure 5. Transmittance data along with fitting to Eq. (1).

Here, the refractive index of the films obey the simple classical dispersion relation for a single oscillator, centered at wavelength  $\lambda_0$ , is expressed by,<sup>25</sup>

$$n^2 = 1 + \frac{(n_0^2 - 1)\lambda^2}{\lambda^2 - \lambda_0^2}, \quad (2)$$

where  $n_0$  is the infinite wavelength refractive index. The absorption coefficient ( $\alpha$ ) is expressed as :

$$\alpha = (e^{a_1 + a_2/\lambda}) + (a_3 + a_4/\lambda + a_5/\lambda^2), \quad (3)$$

where  $a_1$  to  $a_5$  is fitting parameters. The first term in equation 3 is relating to Urbach relation<sup>24</sup>, which represent the absorption edge of intrinsic semiconductor. While the second term is polynomial approximation of absorption resulting from impurity, defects or multi-phonon absorption<sup>18</sup>.

Table2. Optical results.

Film number	Thickness (nm)	Surface roughness (nm)	Refractive index (Eq. 2)		Optical energy gap (eV)
			$n_0$	$\lambda_0$	
I	288	20.1	2.446	287.1	2.676
II	296	20.4	2.473	266.9	2.668
III	324	20.3	2.498	232.6	2.656
IV	356	17.3	2.507	234.0	2.628

Figure 5 shows the transmittance data along with fitting curve of film II. The transmittance fitting results are listed in table 3. No observable change in the surface roughness in case of the films in which immersed for short time ( film II and III) . However a small decrease in the surface roughness was observed, in case of film IV. This decrease could be due to etching of the film surface, after exposing to the solution for long time. This fact was seen clearly in case of immersion of the films for very long time at high solution temperature. In this case pin-holes appear clearly in the films. Moreover increasing of the films refractive index, in NIR region of optical spectra, as function of immersion time, i. e.

increase of ag concentration in the films, are also observed. These small changes could be attributed to the presence of small impurities added.

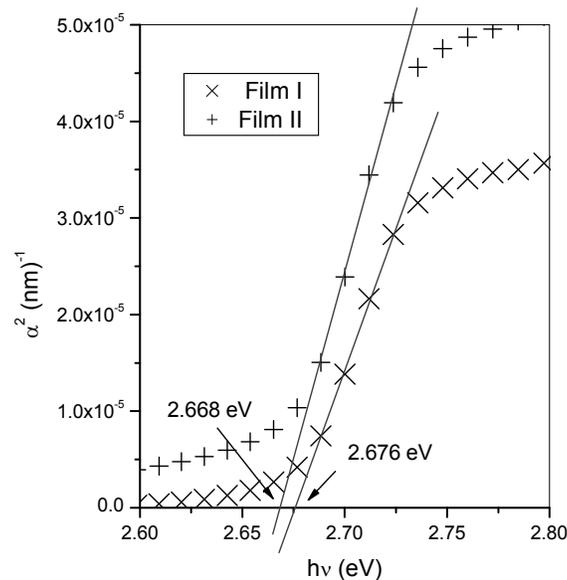


Figure 6. Plot of  $\alpha^2$  vs. photon energy.

Near the absorption edge the optical energy gap ( $E_g$ ) for allowed direct transition can be calculated, using the well-known dependence  $\alpha h\nu \sim (h\nu - E_g)^{1/2}$ . The absorption coefficient, near the absorption edge, was calculated by numerical solution of Eq. 1, using the fitting results for  $d$ ,  $\sigma$  and  $n$ . The energy gap is obtained by extrapolating  $(\alpha h\nu)^2$  against incident photon energy ( $h\nu$ ) plot, as shown in Figure 6. The results of the optical energy gap are also listed in Table 3. The optical energy gap of as-deposited film is around 2.68 eV, while its dropped to 2.63 eV in case of film IV. Decrease of the optical energy gap is observed for immersed films. This indicates that high doping may occurred to this film, leads to a prominent shift in the optical energy gap.

#### 4. CONCLUSIONS

ZnSe thin films are prepared by low-cost simple technique (CSS). Low resistive silver doped films was achieved by an ion exchange process (immersion the post prepared films in  $\text{AgNO}_3$ ). All ZnSe films were cubic in structure with [111] preferred orientation. No peaks, related to Ag or  $\text{Ag}_2\text{Te}$ , appear in the x-ray diffraction pattern, while the EDX results confirm the presence of Ag in the film. The decreasing of Zn concentration in the films, as Ag increased, leads to verify that Ag replaced Zn. The resistivity of the films reduced considerably after immersion in  $\text{AgNO}_3$  solution. No considerable change in the surface roughness was observed. The films lose their transparency as the immersion time increases. Increase of the films refractive index, in NIR region of optical spectra, and small blue shift of optical band gap are also observed. Controlling of immersion time is important parameter to improve the electrical conductivity of the films without undesirable change in their optical properties.

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