OPTOELECTRONIC PROPERTIES OF ZINC SELENIDE (ZnSe) THIN FILMS DEPOSITED USING CHEMICAL BATH DEPOSITION (CBD) TECHNIQUE

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Abstract

Thin films of Zinc Selenide (ZnSe) were deposited on glass substrate at room temperature by Chemical Bath Deposition (CBD) Technique. The sources of Zn and Se were respectively $ZnSO_4$ *and* Na_2SeSO_3 *while NaOH was employed as complexing agent. The deposited sample slides were annealed in an oven at temperatures of* 200^oC*,* 300^oC *and* 400^oC*. The samples were characterized for optical band gap using Spectrophotometer (Janway 6405 UV-VIS Model) by measuring the optical absorption and transmission and Photo conductivity by using the two point probe method in which silver paint was used for attaching two copper wires (as electrodes) on the sample. The estimated band gaps are 2.89eV, 2.95eV, 3.08eV and 3.05eV for the as-deposited and the annealed thin films at temperatures of* 200^oC*,* 300^oC *and* 400^oC *respectively. Annealing increases band gap energy slightly as substrate temperature increases from room temperature to* 400^oC *which indicate blueshifts from the normal bulk value, while the photo and dark currents of the sample annealed at* 300^o *were observed to increase linearly with the applied electric field, but the former being large and the latter is less, which is an indication of positive photoconductivity.*

Key words: *thin films, ZnSe, CBD, Band gap, Photoconductivity*

INTRODUCTION:

The group II-VI Compound Semiconductor materials have attracted great attention in the past decades because of their potential applications in the area of Optoelectronic devices, Solar cells, IR detectors lasers etc. Zinc Selenide is a well-known II-VI Semiconductor compound. It has cubic and/or hexagonal crystal structure, it has Optical band gap in the range 2.6-3.1eV, it has electrical resistivity of the order 10^4-10^{12}Ωcm and the films are yellow-orange in colour [1]. Various techniques have been employed to prepare thin films of ZnSe, including electrodeposition technique [2-4], Metal Organic Chemical Vapour Deposition [5-6], Inert Gas Condensation method [7], Coevaporation method [8],Thermal Evaporation [9-10], Vacuum Evaporation [11], Chemical Bath Deposition (CBD) ([12-17], Molecular Beam Epitaxy [18], Successive Ionic Layer Adsorption and Reaction [19], Cyclic Voltametry method [20] etc. Among the various other methods, Chemical Bath Deposition is found to be simple, convenient, cost effective, and capable of producing uniform and homogeneous thin films to industrial scale. In the pesent work, ZnSe thin films were deposited on glass substr ates using the Chemical Bath Deposition (CBD) technique. The deposited films were annealed and Characterized for their Optical and Electrical properties.

EXPERIMENTAL DETAILS:

Thin films of Zinc Selenide (ZnSe) were deposited on to commercial glass slides ($26x76x2mm^2$) using the Chemical Bath Deposition (CBD) technique. All chemicals used were of Analytical Grade. Before the deposition, the glass slides were rinsed with distilled water, washed with detergent and then rinsed with distilled water. The glass slides were again degreased with ethanol, rinsed with distilled water and then dried in an oven. This process was carried out to ensure clean surface essentially for the formation of nucleation centres that is required for thin film deposition. The deposition was carried out when 5ml (1M) Zinc Sulphate was placed in 50ml glass beaker and 5ml NaOH was added with constant stirring. Addition of excess NaOH reduced the concentration of Zn^{2+}. 3ml (1M) Na_2SeSO_3 was slowly added as a source of selenium (Se) to the mixture. The resulting solution was made up to 50ml with the addition of distilled water and stirring with glass rod for few minutes. The pH of the mixture was maintained at 11 ± 1 confirming the alkalinity of the bath. Clean glass slides were inserted into the bath and held vertically in a synthetic foam cover. The deposition was allowed to take place for 48 hours at room temperature after which the coated slides were withdrawn from the the bath, rinsed with distilled water and dried in air. The as-deposited sample slides were annealed in an oven at temperatures of 200°C, 300°C and 400°C. The samples were characterized for optical band gap using Spectrophotometer (Janway 6405 UV-VIS Model) by measuring the optical absorption and transmission and the Photo conductivity was measured using the two point probe method in which silver paint was used for attaching two copper wires (as electrodes) on the sample. Series connection of D.C power source, a Pico ammeter (Keithley 485) and the sample film was done. The dark current of the sample was measured by covering the sample in a black box while the photocurrent was measured by focussing a filtered white light from a tungsten lamp (200W) on to the sample through a transparent glass window. The field – dependent dark and photocurrent were measured using the Pico ammeter by varying the applied and corresponding current in the circuit.

THEORETICAL CONSIDERATION AND CALCULATION:

Optical: The transmittance (T) can be calculated from the relationship [21];

$$A = \log\frac{1}{T} \tag{1}$$

Where A is the absorbance and T is given [21]:

$$T = \frac{1}{10^{A}} \tag{2}$$

The reflectance (R) is calculated from the relation [21];

$$A + R + T = 1 \tag{3}$$

Or

$$R = 1 - (A + T) \tag{4}$$

The absorption coefficient (α) can be calculated from the observed absorbance data using Beer Lanbert's formular [22] given by;

$$\alpha = 2.303\left(\frac{A}{d}\right)$$

or $$\alpha = \frac{(h\upsilon - E_g)^{1/2}}{h\upsilon} \tag{5}$$

Where A is the total optical absorbance and d is the thickness of the film.

The photon energy, E, is given [21] by:

$$E = h\nu \tag{6}$$

Where h is the Plank`s Constant and ν is the frequency of the photon.

Similarly,

$$E = \frac{hc}{\lambda} \tag{7}$$

Where c is the speed of light and λ is the wavelength. Substituting for constants in equation (7) gives:

$$E = \frac{12{,}400}{\lambda}\text{eV} \tag{8}$$

For semiconductors (where $K^2 << n^2$) there exist a relationship between R and n [23] given by:

$$R = \frac{(n+1)^2}{(n-1)^2} \tag{9}$$

Where R is the reflectance and n is the refractive index.

And the relation between K and α [21] given by;

$$K = \frac{\alpha\lambda}{4\pi} \tag{10}$$

Also, the relationship existing between R, K and n is given [22] by;

$$n = \left(\frac{1+R}{1-R}\right) = \sqrt{\frac{4R}{(1-R)^2} + K^2} \tag{11}$$

Where n is the refractive index, K is the extinction coefficient and R is the optical reflectance.

Electrical: In a homogeneous material, Conductivity is expressed [24] as:

$$\sigma = e(n\mu_n + p\mu_p) \tag{12}$$

Where n and p are the densities of free electron and holes, and μ_n/μ_p are the electron/hole mobility. For the same material under equilibrium condition n and p are uniform throughout the material and photoconductivity occurs when the values of n and p are enhanced due to photon absorption. Hence,

$$\Delta\sigma = e\ (\Delta n\mu_n + \Delta p\mu_p) \tag{13}$$

The impinging light intensity on the material along the z – axis is I_o [in J/(s cm^3)], and n(x,y,z,t), p(x, y, z, t) are the non-equilibrium electron and hole densities [in 1/cm^3], respectively, generated by the in-coming photons. The continuity equations are expressed by their general form [25];

$$\frac{\partial n}{\partial t} = +\frac{1}{e}\nabla\ *\ \vec{J}_n - \frac{n}{\tau_n} + \eta\,\frac{I_o}{\hbar\omega}\alpha\exp\,(-\alpha z) \tag{14}$$

$$\frac{\partial n}{\partial t} = -\frac{1}{e}\nabla\ *\ \vec{J}_p - \frac{p}{\tau_p} + \eta\ \frac{I_o}{\hbar\omega}\alpha\exp\,(-\alpha z) \tag{15}$$

Where the terms n/τ_n and p/τ_p represent the recombination rates for the electrons and holes, and τ_n and τ_p as their respective lifetimes. The term $\frac{I_o}{\hbar\omega}\alpha\exp\,(-\alpha z)$ is the decay of the generation rate along the penetration of light of the non-equilibrium carriers, $\hbar\omega$ is the impinging light energy and α is the absorption coefficient, η is the unit less conversion efficiency coefficient, and e the elementary charge. The vectors j_n and j_p are the electron and hole components of the current density and are given [25] by;

$$\vec{J}_n = \vec{J}_{n,E} + \vec{J}_{n,D} = eN\mu_n\vec{E} + eD_e\nabla n \tag{16}$$

$$\vec{J}_p = \vec{J}_{p,E} + \vec{J}_{p,D} = eN\mu_p\vec{E} - eD_h\nabla p \tag{17}$$

Where$\vec{J}_{n,D}$, $\vec{J}_{p,D}$ stands for diffusion current driven by the density gradient and $\vec{J}_{n,E}$, $\vec{J}_{p,E}$ represents the conduction current driven by an external electric field $\vec{E}$.The terms $D_e\nabla n$ and $D_h\nabla p$ refers to the diffusion of the non-equilibrium carriers, whereas D_e and D_h, are diffusion constants of electrons and holes respectively. The drift mobility of electrons and holes is μ_n and μ_p and the total electron and hole densities are N and P, which are given [25] by;

$$N = N_o + n \tag{18}$$

$$P = P_o + p \tag{19}$$

Where N_o and P_o are the electron and hole equilibrium uniform densities. Hence, total current density (from 16 and 17) is given [25] by;

$$\vec{J} = \vec{J}_{dark} + \vec{J}_{ph} \tag{20}$$

Where,

$$\vec{J}_{dark} = e\ (N_o\mu_n + P_o\mu_p)\ \vec{E} \tag{21}$$

and

$$\vec{J}_{ph} = e\ (n\mu_n + \mu_p)\vec{E} + e\ (D_e\nabla n - D_h\nabla p) \tag{22}$$

On assuming the following conditions:

i. n = p, i.e. the local neutrality condition implying that, $\tau_n = \tau_p = \tau$ (equal times of electrons and holes).

ii. N_o and P_o are uniform and time independent, i.e., $\partial N_o/\partial t = \partial P_o/\partial t = \nabla N_o = \nabla P_o = 0$.

iii. $\nabla\cdot\ \vec{E} = 0$ under condition (i) above.

Putting the current density $\vec{J}_n$ and $\vec{J}_p$ into (14) and (15) gives [25];

$$\frac{\partial n}{\partial t} = +D_e\,\nabla^2 n - \frac{n}{\tau} + \eta\,\frac{I_o}{\hbar\omega}\alpha\exp\left(-\alpha z\right) + \mu_n\vec{E}\cdot\nabla n \tag{23}$$

$$\frac{\partial p}{\partial t} = +D_h\,\nabla^2 p - \frac{p}{\tau} + \eta\,\frac{I_o}{\hbar\omega}\alpha\exp\left(-\alpha z\right) + \mu_p\vec{E}\cdot\nabla p \tag{24}$$

Multiplying (23) and (24) with the electron and hole conductivity, i.e., σ_n and σ_p respectively, and, by adding both equations and simultaneously replacing n and p (since n=p) gives the following relationship:

$$\frac{\partial n}{\partial t} = \frac{\sigma_p D_e + \sigma_n D_h}{\sigma_n + \sigma_p}\nabla^2 n - \frac{n}{\tau} + \eta\,\frac{I_o}{\hbar\omega}\alpha\exp(-\alpha z) + \frac{\mu_n\sigma_p - \mu_p\sigma_n}{\sigma_n + \sigma_p}\vec{E}\cdot\nabla n \tag{25}$$

The bipolar diffusion coefficient is defined [25] as,

$$D = \frac{\sigma_p D_e + \sigma_n D_h}{\sigma_n + \sigma_p} \tag{26}$$

The bipolar drift mobility μ_E is defined [25] as,

$$\mu_E = \frac{\mu_n\sigma_p - \mu_p\sigma_n}{\sigma_n + \sigma_p} \tag{27}$$

And is different from the bipolar diffusion mobility μ_D, which is defined [25] as,

$$\mu_D = \frac{\mu_n\sigma_p + \mu_p\sigma_n}{\sigma_n + \sigma_p} \tag{28}$$

Thus, the continuity equation for n (and consequently for p, since n=p),

$$\frac{\partial n}{\partial t} = D\nabla^2 n - \frac{n}{\tau}\frac{\eta I_o}{\hbar\omega}\alpha\exp(-\alpha z) + \mu_E\vec{E}\cdot\nabla n \tag{29}$$

And for the photocurrent density:

$$\vec{J}_{ph} = e\left(\mu_n + \mu_p\right)n\vec{E} + e(D_e - D_h)\nabla n \tag{30}$$

RESULTS AND DISCUSSIONS:

The deposition of ZnSe thin films occurs when the ionic product of Zn^{2+} and Se^{2-} ions exceeds the solubility product of ZnSe. The control of Zn^{2+} and Se^{2-} ions in the Bath controls the rates of precipitation and the film formation and the equations of the deposition process is given [15] as follows:

The hydrolysis of sodium Selenosulphate (Na_2SeSO_3) in the bath to give Se^{2-} ions the following reactions:

$$Na_2SeSO_3 + OH^- \rightleftharpoons Na_2SO_4 + HSe^- \tag{31}$$

$$HSe^- + OH^- \rightleftharpoons H_2O + Se^{2-}. \tag{32}$$

The reaction between Zn^{2+} and NaOH takes place through:

$$ZnSO_4 + 2NaOH \rightleftharpoons Zn(OH)_2 + Na_2SO_4 \tag{33}$$

When the NaOH is added to the Zn^{2+} salt solution, the $Zn(OH)_2$ begin to precipitate when the solubility product (SP) of $Zn(OH)_2$ is exceeded, i.e

$$Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2 \tag{34}$$

The Zn $(OH)_2$ precipitate dissolves in excess NaOH solution to form the complex sodium zinc hydroxide Na_4Zn $(OH)_6$ as follows:

$$Zn^{2+} + 4NaOH \rightleftharpoons Na_4Zn(OH)_6 \tag{35}$$

$$Na_4Zn(OH)_2 \rightleftharpoons 4Na^+ + HZnO_2^- + 3OH^- + H_2O. \tag{36}$$

Finally, the ZnSe thin film formation takes place through:

$$HZnO_2^- + HSe^- \rightleftharpoons ZnSe + 2OH^-. \quad (37)$$

Fig. 1. Shows the plots of $(\alpha h\nu)^2$Vs $h\nu$ estimating the band gaps for both the as-deposited and the annealed thin films of ZnSe at varied temperatures (i.e 200°C, 300°C and 400°C). The energy band gaps estimated by extrapolating the straight line portion of the plots for zero absorption coefficient values which gives an absorption energies corresponding to the band gap energies. The estimated band gaps are 2.89eV, 2.95eV, 3.08eV and 3.05eV for the as-deposited thin film and the annealed thin films at temperatures of 200°C, 300°C and 400°C respectively. The band gap energy increases slightly as substrate temperature increases from room temperature to 400°C which indicates blueshifts from the normal bulk value and confirming that, annealing the films causes a redshifts of 0.19eV, 0.25eV, 0.38eV and 0.35eV in the optical spectra to that of characteristic bulk ZnSe [15] and could be attributed to size quantization leading to quantum confinement of ZnSe thin film [26].

Fig. 2. Shows the plots of currents (Dark and Photo) against the applied electric field which was used in analysing the photoconductivity of the ZnSe thin film annealed at 300°C. Both the photo and dark currents were observed to increase linearly with the applied electric field, but the former being large and latter is less, which is an indication of positive photoconductivity which is caused by the generation of mobile charge carriers caused by absorption of photons. This is in agreement with the result of [27]. Since illumination produces electron-hole pairs and the holes neutralize the repulsive potential at the grain boundaries which leads to an exponential increase in the electron mobility that gives a high photo current under illumination, combined with the low dark current, it produces a high photosensitivity in the thin films [6].

CONCLUSION:

ZnSe thin films were deposited on glass substrates using the Chemical Bath Deposition (CBD) technique. The as-deposited sample slides were annealed in an oven at temperatures of 200°C, 300°C and 400°C and then characterized for their optical and electrical properties. Annealing the films causes a redshifts of 0.19eV, 0.25eV, 0.38eV and 0.35eV in the optical spectra to that of the characteristic bulk ZnSe and this was attributed to size quantization leading to quantum confinement of ZnSe thin film and the photo and dark currents were observed to increase linearly with the applied electric field, but the former being large and latter is less, which is an indication of positive photoconductivity which is caused by the generation of mobile charge carriers caused by absorption of photons.

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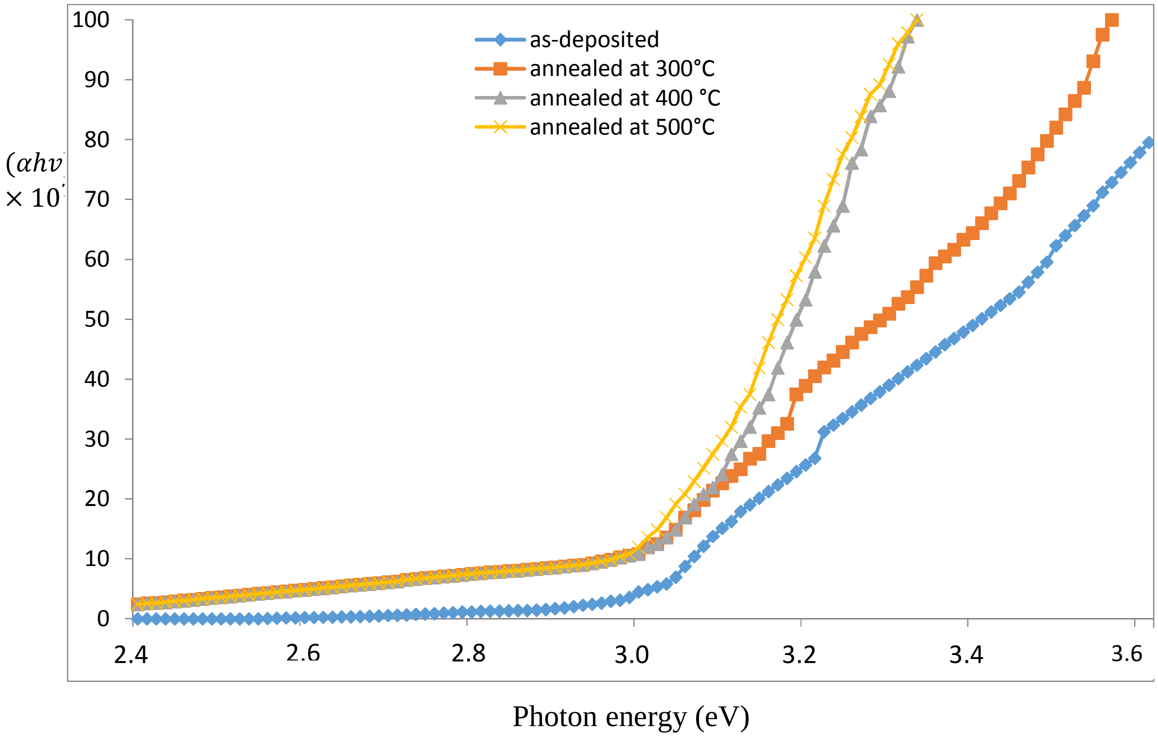
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Photon energy (eV)

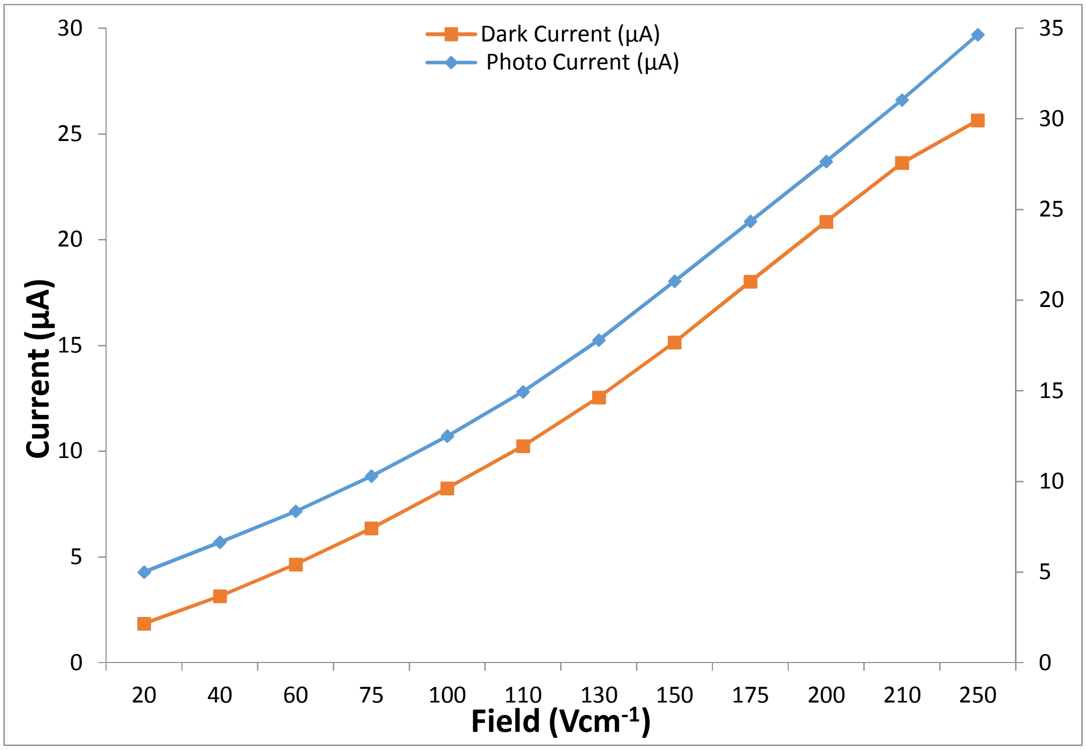

Figure 2: Photoconductivity study of ZnSe Thin films