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EFFECT OF THE SUBSTRATE TEMPERATURES ON THE OPTICAL PROPERTIES OF THE $Cd_{0.22}Zn_{0.78}S$ THIN FILMS BY SPRAY PYROLYSIS METHOD

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Abstract. $Cd_xZn_{1-x}S$ films are of considerable interest for a variety of solar cell systems in which CdS films have been demonstrated to be effective as the large band gap window material of a heterojunction. $Cd_{0.22}Zn_{0.78}S$ films have been deposited onto the glass substrates at different substrate temperatures of 250°C, 275°C, and 300°C. The average optical transmittance all of the films was over 70% in the visible range. The optical absorption studies reveal that the transition is direct with band gap energy values between 3.012 and 3.095eV. The optical constants such as refractive index and dielectric constant of the thin films were determined. The important changes in absorption edge, refractive index and the dielectric constant were observed due to the substrate temperature. The refractive index dispersion curves of the films obey the single oscillator model and oscillator parameters changed with substrate temperature. The most significant result of the present study is to indicate that substrate temperature of the films can be used to modify in the optical band gaps and optical constants of the $Cd_{0.22}Zn_{0.78}S$ thin films.

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1. INTRODUCTION

In recent years, extensive studies have been carried out on the preparation and characterization of wide band gap oxide semiconductors such as TiO_2, ZnO, SnO_2, [1-3], etc. due to their application in photovoltaic, photoelectrochemical energy conversion and photoconductors. The cadmium zinc sulfide (CdZnS) thin film is one of the promising materials in this respect. CdZnS thin films have been widely used as a wide band-gap window material in heterojunction solar cells and in photoconductive devices. The CdZnS has been prepared by various methods such as vacuum evaporating, screen printing, sintering, chemical deposition, physical vapor deposition, spray pyrolysis, electrodeposition [4-6]. Among these, the spray pyrolysis method is cheaper, simpler and more versatile than the others and gives the possibility of obtaining films with suitable properties for optoelectronic applications and also when large areas are needed.

The study of optical absorption has proved to be very useful for elucidation of the electronic structure of these materials. It is possible to determine indirect and direct transition occurring in band gap of the materials by optical absorption spectra. The data transmittance can be analyzed to determine optical constants such as refractive index, extinction coefficient and dielectric constant. The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design.

The optical constants of thin films depend on the condition of preparation such as the substrate temperature during the deposition process. These parameters have to be controlled right from the initial stages of deposition. In this work, the effect of the substrate temperatures on the optical properties of $Cd_{0.22}Zn_{0.78}S$ thin films are presented and discussed.

2. EXPERIMENTAL

Spray pyrolysis is basically a chemical process, which consist of a solution that is sprayed into a substrate held at high temperature, where the solution reacts forming the desired thin film. $Cd_{0.22}Zn_{0.78}S$ thin films were deposited on thoroughly pre-cleaned glass substrates by using spray pyrolysis method. In this method, the film precursor is sprayed into a heated substrate (T=250°C, 275°C, and 300°C) using nitrogen as carrier gas. Cadmium chloride dehydrate, zinc chloride and thiourea were used as the starting material. The spray pyrolysis deposition system was given in details elsewhere [7-8]. The adhesion of the films onto the substrates was quite good. $Cd_{0.22}Zn_{0.78}S$ thin film exhibited yellow colour. The thickness of deposited all the thin films was measured by weight difference method using a sensitive semi-microbalance. These films, i.e., deposited at 250°C, 275°C and 300°C substrate temperatures were named as S1, S2 and S3, respectively.

The optical absorption and transmittance spectra of all the thin films at room temperature were recorded on a SHIMADZU UV-2450 UV-VIS Spectrophotometer in the wavelength range 190nm-900nm. The reflectance data were calculated using these data.

3. RESULTS AND DISCUSSION

3.1 Optical band gap of the thin films

In order to determine the optical band gap of these films, the absorbance spectra of the films were recorded at room temperature. The transmission and reflection spectra of S1, S2 and S3 thin films are shown in Fig. 1 (a-b). The optical band gap can be calculated from the following relationship [9],

$$(\alpha h\nu) = A(h\nu - E_g)^m \qquad (1)$$

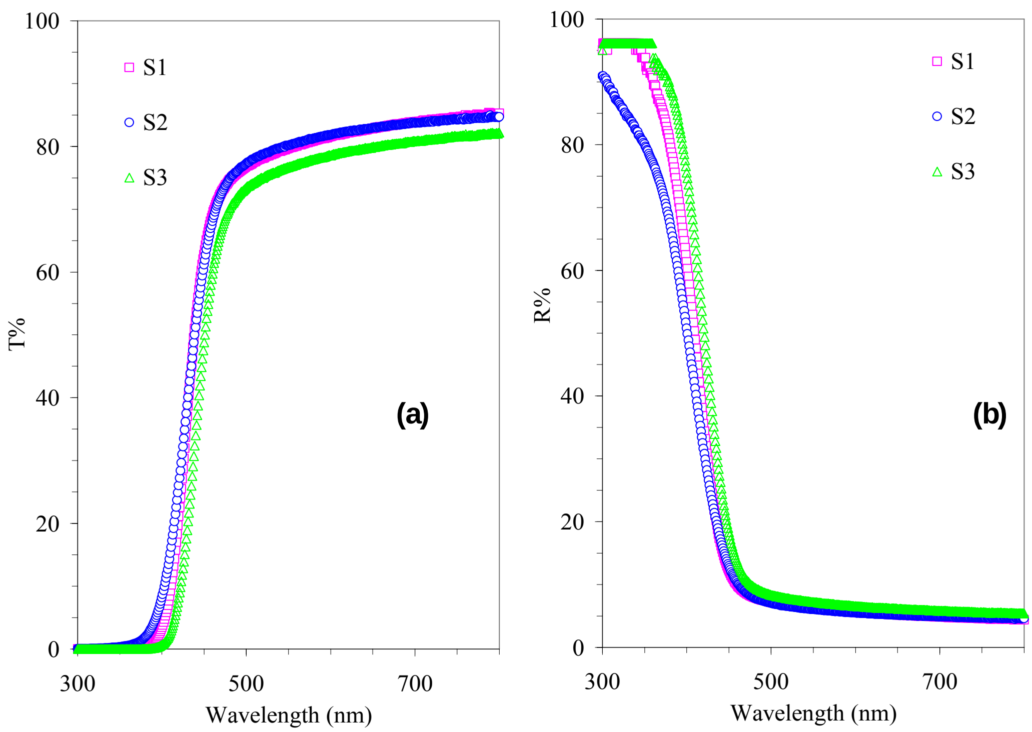

Fig. 1. Transmittance (a) and reflectance (b) spectra of the thin films.

where m is a constant which determines type of the optical transition (m=1/2 for allowed direct transitions and m=2 for allowed indirect transitions). Here, the direct transitions are optical transitions that occur in the semiconductors. It is well known that direct transition across the band gap is feasible between the valence and the conduction band edges in k space. In the transition process, the total energy and momentum of the electron-photon system must be conserved. Fig. 2 shows plot of $(\alpha h\nu)^2$ vs. photon energy. The values of the direct band gap E_g were determined by a least squares fit and are given in Table 1. E_g values change with the substrate temperatures.

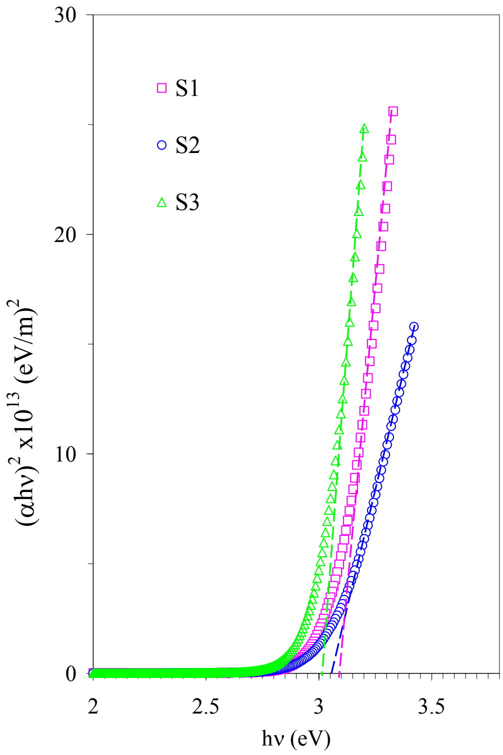

Fig. 2. The plots of the variations of $(\alpha h\nu)^2$ vs. $(h\nu)$ for the thin films.

Table 1.

Film	**E_g (eV)**
S1	3.095
S2	3.052
S3	3.012

3.2. The refractive index and dielectric constants of the thin films

The complex refractive index and dielectric function characterize the optical properties of any solid material. The dispersion plays an important role in the research for optical materials. Because, it is a significant factor in optical communication and in designing devices for spectral dispersion. The complex refractive index of the film is expressed as [10],

$$\hat{n} = n(\omega) + ik(\omega) \,, \tag{2}$$

where n is the real part and k is the imaginary part of complex refractive index. The refractive index of the thin films can be determined from the following equation [11],

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \tag{3}$$

where k ($k=\alpha\lambda/4\pi$) is the extinction coefficient. The refractive index values of the thin films were calculated using Eq.3. The refractive index and extinction coefficient k dependence of wavelength were plotted. These constants at 450 nm are given in Table 2. The fundamental electron excitation spectrum of the films was described by means of a frequency dependent of the complex electronic dielectric constant. The dielectric constant is defined as, $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$ and real and imaginary parts of the dielectric constant are related to the n and k values. The ε_1 and ε_2 values were calculated using the formulas [10],

$$\varepsilon_1 = n^2 - k^2, \tag{4}$$

$$\varepsilon_2 = 2nk, \tag{5}$$

ε_1 and ε_2 values at 450 nm are given in Table 2.

Table 2. Optical constant of the thin films (at 450nm).

Film	n	kx10^{-2}	ε_1	ε_2 x10^{-2}
S1	2.08	1.21	4.34	5.02
S2	2.13	1.28	4.52	5.43
S3	2.50	1.86	6.25	9.31

3.3. Single Oscillator Parameters from WDD Model

According to the single oscillator model proposed by Wemple and DiDomenico [12] the optical data could be described to a very good approximately by the following formula

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \tag{6}$$

where, n is the refractive index, E_o is the average excitation energy for electronic transitions, $h\nu$ is the photon energy and E_d is the so–called dispersion energy. The latter quantity measures the average strength of the interband optical transitions. Plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ allows the determination of the oscillator parameters by fitting a straight line to the points (Fig. 3).

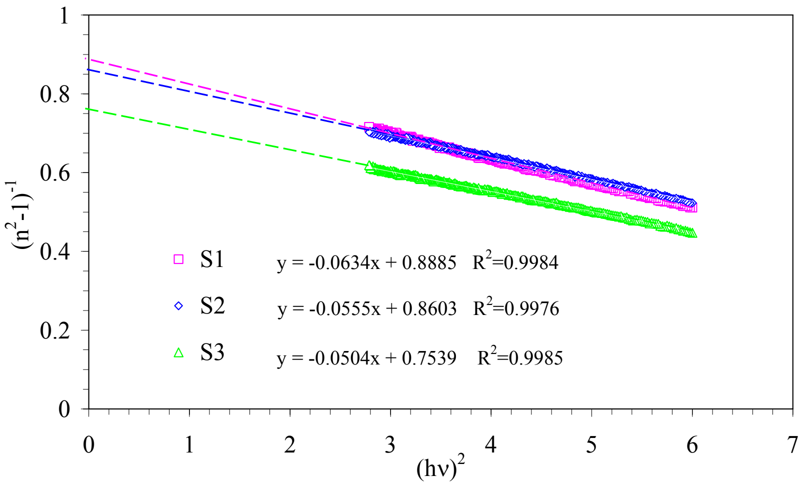

Fig. 3. The plots of the variations of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for the thin films.

The value of E_o and E_d can be directly determined from the slope $(E_oE_d)^{-1}$ and the intercept on the vertical axis, (E_d / E_o). The values obtained for the dispersion parameters, E_o and E_d are tabulated in Table 3. The oscillator energy, E_o is an average energy gap as pointed out in many references [13-19]. We found that E_o value of the films is related empirically to the lowest direct band gap by $E_o \approx 1.2\ E_g$. This relation is in agreement with the obtained relation ($E_o \approx 1.4\ E_g$) obtained from the single oscillator model [13]. The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the relationship

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad \text{and} \quad E_d^2 = \frac{M^3{}_{-1}}{M_{-3}}. \tag{7}$$

The obtained values are given in Table 3.

Table 3.

Film	E_o (eV)	E_d (eV)	M_{-1}	M_{-3} (eV)$^{-2}$
S1	3.744	4.213	1.125	0.080
S2	3.937	4.576	1.162	0.075
S3	3.868	5.130	1.326	0.089

4. CONCLUSIONS

The effects of substrate temperatures on optical properties of $Cd_{0.22}Zn_{0.78}S$ thin film deposited onto glass substrates by the spray pyrolysis method have been investigated. The direct optical band gaps of the films were found to be between 3.012 and 3.095eV. The refractive index and the dielectric constants of the films changed with substrate temperature. The refractive index dispersion curves of the films obey the single oscillator model.

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ЕФЕКТ НА ТЕМПЕРАТУРИТЕ НА СУПСТРАТОТ ВРЗ ОПТИЧКИТЕ СВОЈСТВА НА $Cd_{0.22}Zn_{0.78}S$ ТЕНКИ ФИЛМОВИ СО МЕТОД НА СПРЕЈ ПИРОЛИЗА

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Апстракт. Филмовите од $Cd_xZn_{1-x}S$ е нанесен на стаклен супстрат при различни температури на стаклото и тоа: 250°C, 275°C и 300°C. Средната трансмитанца во видлвиот дел на сите филмови беше над 70%. Ипситувањето на отпичката апсорпција открија дека преминот е директен со широчина на забранетата зона помеѓу 3.012 и 3.095eV. Беа определени оптичките константи на тенките филмови, како што е индексот на прекршување и диелектричната константа. Во зависност од температурата на субстратот беа набљудувани промени во апсорпционите пикови, индексот на прекршување и диелектричната константа. Дисперзионите криви на индексите на прекршување на филмовите се покоруваат на моделот на единечен осцилатор, а параметрите на осцилаторот се менуваат со промена на температурата. Најзначаен резултат на ова истражување е заклучокот дека температурата на субстратот може да се искористи за промена на отпичката забранета зона и оптичките константи на тенките филмови од $Cd_{0.22}Zn_{0.78}S$.