JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1414 - 1417

The effect of deposition parameters on the physical properties of $Cd_xZn_{1-x}S$ films deposited by spray pyrolysis method

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The spray pyrolysis method for the deposition of thin solid films is a good method for the preparation of thin films suitable for scientific studies and for many applications in technology and industry. This method was used for the preparation of thin films of the important semiconductors II-VI. In this work, among these materials $Cd_xZn_{1-x}S$ films were deposited by spray pyrolysis method at 275 ^oC substrate temperature onto glass substrate at different deposition parameters. The structure of the films was analyzed by X-ray diffraction and the results obtained showed that the film structure polycrystalline structure. The effect of different deposition parameters on the band gap and optical constants (refractive index, extinction coefficient, and dielectric constants) of these films has been investigated and the deposition parameters change the optical constants and Urbach energy values of the films. The dispersion parameters such as E_o (single-oscillator energy) and E_d (dispersive energy) of the deposited thin films were determined.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Spray pyrolysis method, Cd-Zn-S, Optical constant, Refractive index, Extinction coefficient, Dielectric constant

1. Introduction

Sulfides of cadmium and zinc have been extensively used as a wide band gap window material in heterojunction solar cells and in photoconductive devices. The CdZnS ternary compound is also potentially useful a window material for the fabrication of p–n junctions without lattice mismatch in the devices based on materials like CdTe [1] or $CuIn_xGa_{1-x}Se_2$ [2]. $Cd_xZn_{1-x}S$ films have been prepared by a variety of methods, which are including spray pyrolysis [3-5], chemically deposited [6], molecular beam epitaxy (MBE) [7], chemical method synthesize [8]. Among these, spray pyrolysis is one of the most used methods. Compared to other methods, spray-pyrolysis has the following advantages; (i) simple and continuous operation, (ii) economical, (iii) uniform particle size distribution, (iv) controllable size, and (v) controllable anion and cation concentrations or dopants.

The knowledge of optical constants of materials is frequently of great interest in the design and analysis of materials to be used in optoelectronics. Moreover, optical measurements are extensively used for characterization of composition and quality of the materials. So, it is essential to have an insight into the optical properties, which include the optical band gap, reflectivity, absorption coefficient, the dielectric constant and the refractive index as a prerequisite in using the suitable material for device applications.

The aim of this study, it is to investigate effect of deposition parameters on structural and optical properties of $Cd_xZn_{1-x}S$ thin films to calculate optical constants such as refractive index and dielectric constant, the Urbach energy E_u and the dispersion parameters such as E_o (single-oscillator energy) and E_d (dispersive energy).

2. Experimental

$Cd_xZn_{1-x}S$ films have been deposited onto the glass substrates at 275 ^oC substrate. The films were deposited by taking equimolar aqueous solutions of $CdCl_2.H_2O$, $ZnCl_2$ and $(NH_2)_2CS$ in a appropriate volume to obtain the Cd:Zn ratio 1:1 and CdZn:S 1:1. The starting solution was mixed thoroughly and final solution was sprayed. During the spraying process, the substrates were heated by electrically heating the copper plate. Nitrogen gaseous was used as a carrier gas. Substrate temperature was controlled by means of Iron-Constantan thermocouple. The other deposition conditions are given in Table 1.The structural properties of all the films were studied by RIGAKU RINT 2200 Series X-Ray Automatic Diffractometer using Cu:K_α radiations ($\lambda_{K\alpha}$=1.5405 Å). The scanning angle 2θ was varied in the range of 20^o-60^o in steps of $2^o min^{-1}$ for all the films. The optical absorption spectra are recorded from 190 to 900 nm wavelength using SHIMADZU UV-2450 PC UV-VIS Scanning Spectrophotometer at room temperature.

Table 1. Deposition parameters of the $Cd_{1-x}Zn_xS$ films.

Material	Spraying Solution Molarite (M)	Solution flow rate (ml/min)	Spraying time (min)
$Cd_{0.22}Zn_{0.78}S$ (S_1)	0.01	3.57	45
$CdZnS_2$ (S_2)	0.05	2.60	80

3. Results and discussion

X-ray diffraction spectra of the $Cd_xZn_{1-x}S$ films are given in Fig. 1. X-ray diffraction spectra of the films were taken at room temperature. X-ray diffraction spectra of the films showed that they are hexagonal and exhibit polycrystalline structure.

The transmittance spectra of the S_1 and S_2 films are shown in Fig. 2.a. The relationship between absorption coefficient and optical band gap is expressed to calculate the band gap of the compounds by the following relationship [9],

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

where A is an energy-independent constant and E_g is the optical band gap and m is a constant which determined type of optical transition. The values of the direct optical band gap E_g were obtained from the intercept of $(\alpha h\nu)^2$ vs. $h\nu$ curves plotted and are given in Table 2. It can be evaluated that the obtained optical band gap values by this method are suitable for many scientific studies and technological applications, such as gas sensors, heat mirrors, transparent electrodes, solar cells and piezoelectric devices.

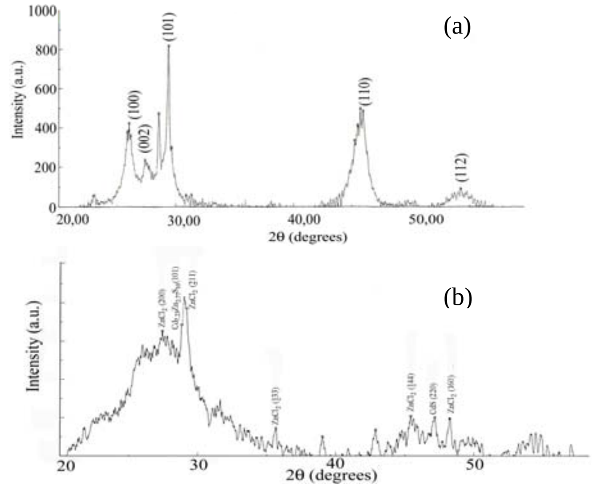
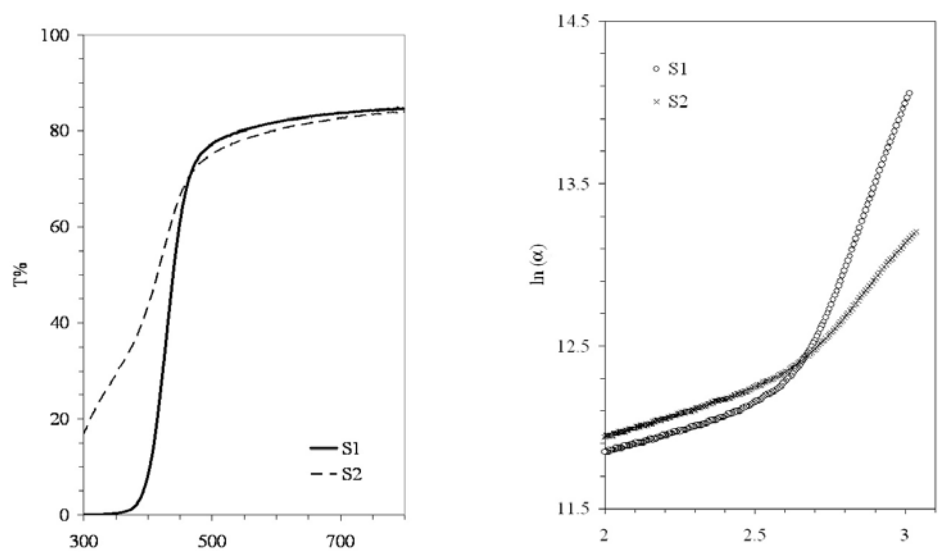


Fig. 1. X-ray diffraction spectra of (a) S_1 (All the peak Belong to $Cd_{0.22}Zn_{0.78}S$) and (b) S_2 films.

The absorption coefficient near the fundamental absorption edge is exponentially dependent on the incident photon energy and obeys the empirical Urbach relation, where $ln\alpha$ varies as a function of $h\nu$. The absorption edge in the spectral range of direct optical transitions has exponential shape following the relationship [10],



(a) (b)

Fig. 2. (a) The transmittance spectra and (b) the Urbach plots of the films.

$$\alpha = \alpha_o \, exp\left(\frac{E}{E_U}\right) \quad (2)$$

where E_U is the Urbach energy, which corresponds to width of the band tail. α_o is a constant. Thus, a plot of $ln(\alpha)$ vs. $h\nu$ should be linear whose slope gives Urbach energy. The Urbach plots of the films are shown in Fig. 2.b. Urbach energy was calculated from the reciprocal gradient of the linear portion of these curves and is given in Table 2. E_U energy values change inversely with the optical band gap. Some defects during formation of film are formed. These defects produce localized states in the films. Thus, the increase in width of the localized states in the optical band gap decreases the optical band gap.

Table 2. Optical constant of the $Cd_{1-x}Zn_xS$ films.

Film	E_g (eV)	E_U (meV)	E_o (eV)	E_d (eV)
S1	3.02	195	3.937	4.576
S2	3.04	495	4.250	13.759

In order to calculate the refractive index of the films, we recorded the reflectance spectra of the films. We calculated the refractive index values of the films using the following equation [11],

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

where R is the reflectance and k is the extinction coefficient. The refractive index dependence on the wavelength is shown in Fig. 3. The refractive index of the films significantly changes with deposition parameters.

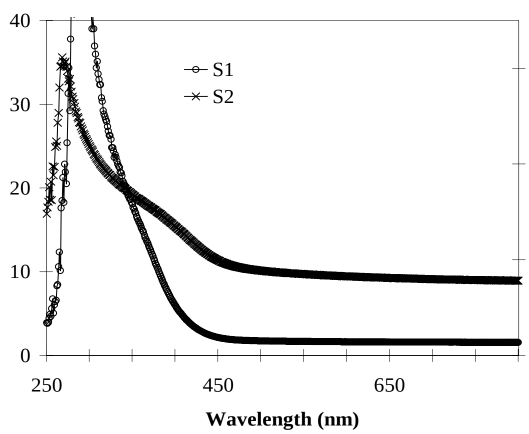


Fig. 3. The refractive index (n) versus of the wavelength.

The single-oscillator parameters were calculated and discussed in terms of the Wemple–DiDomenico model. The dispersion parameters of various materials were investigated by using the model from the literature [12-14]. This model describes the dielectric response for transitions below the optical gap. The dispersion plays an important role in the research for optical materials due to a significant factor in optical communication and in designing devices for spectral dispersion. Below the absorption edge, refractive index dispersion can be analyzed by the single oscillator model [15]

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad (3)$$

where h is Planck's constant, E_o is the average excitation energy for electronic transitions and E_d is the dispersion energy, which is a measure of the strength of interband optical transitions. These parameters can be easily obtained by plotting of $1/n^2-1$ vs. $(h\nu)^2$. The E_d and E_o values was calculated from the slope $(E_dE_o)^{-1}$ and intercept (E_o/E_d) (Table 2). The obtained dispersion parameters change with deposition parameters.

The imaginary and real parts of dielectric constant of the films were also determined by the following relations [16].

$$\varepsilon_1 = n^2 - k^2 \text{ and } \varepsilon_2 = 2nk$$

where $k=\alpha\lambda/4\pi$. The real and imaginary parts of the dielectric constant of the films are respectively shown in Fig. 4 (a-b). It is seen that both ε_1 and ε_2 decreases with increasing wavelength. The real and imaginary parts follow the same pattern and the values of real part are higher than the imaginary parts. The deposition parameters cause important changes in real part and imaginary parts of the dielectric constant of the films.

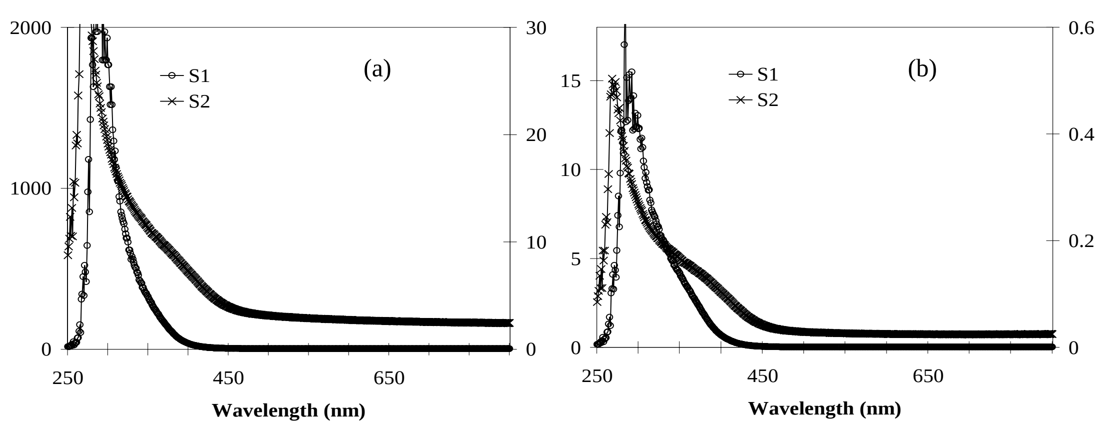


Fig. 4. The real (a) and imaginary (b) parts of the dielectric constant of the films.

4. Conclusions

$Cd_{1-x}Zn_xS$ thin films have been deposited by the spray pyrolysis method at 275 ^oC substrate temperatures for different deposition parameters. The structure of the films was analyzed by X-ray diffraction and the results obtained showed that the film structure is polycrystalline. The spray pyrolyzed thin films show average transmission values are 81% and 80% in the wavelength range 450-800 nm for S_1 and S_2 films, respectively. The optical constants such as refractive index (n), the real (ε_1) and imaginary (ε_2) parts of the dielectric constant of the films were calculated for the films. All of these constants are decreased with wavelength. The optical absorption spectra of the films show that the absorption spectra mechanism is due to direct transitions. The Urbach energies (E_U) were calculated. The optical dispersion (E_o and E_d) using Wemple-DiDomenico model were also analyzed. In conclusion, the influence of the deposition parameters on optical properties of $Cd_{1-x}Zn_xS$ thin films is significant.

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