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Research Article

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Experimental Study on Structural, Optical and Electrical Properties of Chemical Bath Deposited CdZnS Thin Films

Sabbir Akhanda*, Rummana Matin, Muhammad Shahriar Bashar, Abu Kowsar, Mashudur Rahaman and Zahid Hasan Mahmood

Department of Electrical and Electronics Engineering, Dhaka University, Bangladesh

Abstract

CdZnS thin films have been prepared from an aqueous solution containing cadmium chloride, zinc acetate and thiourea by chemical bath deposition (CBD) method on a glass substrate at 82°C. Amount of cadmium chloride and zinc acetate were systematically varied as y=0.2, 0.4, 0.6, 0.8 (y=a/(a+b), a=volume of zinc acetate, b=volume of cadmium chloride) and subsequent effects on the film's property were studied by diffractometer, scanning electron microscope, spectrophotometer, four point probe and hall effect measurement. X-ray diffraction result shows that an increase in the Zn-content decreases the crystalline quality of the films. Transmittance and absorbance data was obtained by using UV-Vis spectrometer. Transmittance of 85-90% is found beyond the 700 nm wavelength. Optical bandgaps calculated from these data show a gradual increase in value with a gradual increase in Zn content. The electrical resistance of the so prepared films were measured by four point probe method. The result indicates that the resistance increases with increasing Zn content.

Keywords: Chemical bath deposition; Thin film solar cell; CdZnS; X-ray diffraction; Scanning electron microscope; UV-visible spectrometry

Introduction

Thin film solar cell is a major branch of solar cell research due to its potential application in cost reduction. Selection of window layer material plays an important role in the overall performance of a thin-film solar cell. Wider bandgap and higher optical transmittance are two fundamental properties a material must possess to act as a window layer in a solar cell. CdS is the most widely used window material now-a-days. But, CdS absorbs the blue portion of the sunlight and decreases the short-circuit current of the solar cell. CdZnS is a promising candidate for replacing CdS as a window layer [1]. Its optical bandgap is relatively wider than CdS and can be tuned from 2.42-3.60 eV by the controlled addition of Zn [2]. It also provides higher optical transmittance than CdS that in turn increases the short-circuit current of the solar cell [3-6].

Various thin-film deposition technique like vacuum evaporation, spray pyrolysis, dip technique, electrodeposition, chemical bath deposition (CBD), SILAR has been used to synthesize CdZnS thin films [7-11]. Among these deposition techniques, CBD is widely accepted as the preferable method to synthesize CdZnS thin film. It is practically the simplest and the cheapest method that yields a stable, uniform, adherent hard film under a non-vacuum condition. Jiyon et al. prepared CdZnS thin film using 30% Zn content in bath solution by this method. They reported that the films had 80% transmittance and optical bandgap within 2.40-2.70 eV [12]. Ravangave et al. used cadmium chloride, zinc chloride and thiourea as the precursor solution for CBD and achieved 78% transmittance in the visible region for x=0.8 [13]. 75-85% transmittance was achieved by CBD using a precursor solution of cadmium acetate, zinc acetate and thiourea [14]. In this work, we used cadmium chloride, zinc acetate, thiourea as the precursor solution and presented a chemical bath deposition route that can increase the transmittance of the films to 85-90% and also clearly illustrated the effect of varying Zn-content on the properties of CdZnS thin films.

Materials and Methods

CdZnS thin film was deposited on a sodalime glass substrate. The chemicals used were cadmium chloride (0.15 M), zinc acetate (0.15 M) and thiourea (0.3 M). These chemicals were mixed in a 150 ml beaker. Four beaker was thus prepared but each had different volume proportion of chemicals (Y=0.2, 0.4, 0.6 and 0.8) as shown in Table 1.

pH of each set was adjusted to 10-11.5 by adding 30% aqueous solution of NH_3. All the chemicals were of analytical grade. The solution sets were then placed in a CBD setup and temperature was maintained at 82°C. The substrates were cleaned with acetone, methanol and DI water. Acetone was used to remove organic impurities from the glass substrates, particularly for dissolving oily or greasy contaminants. Finally, two glass slides were placed vertically inside each reaction beaker with the help of the substrate holders. A magnetic stirrer bar was used in each beaker for better mixing. These beakers were removed from the CBD system after 20 minute. Thin yellowish films were obtained on the glass slides at the end of the process. Then each glass slides were washed with distilled water. They were then annealed at 200°C in N_2 atmosphere for 1 hour.

The crystallinity of the films was tested by BRUKER D8 X-ray diffractometer. High magnification image of the films were taken with a 6490 jeol jsm model scanning electron microscope (SEM). The optical characteristics were measured by UH4150 spectrophotometer. Four point probe and hall measurement was used to investigate the electrical properties of the films.

Result

XRD patterns in Figure 1 confirms the formation of the CdZnS

***Corresponding author:** Sabbir Akhanda, Department of Electrical and Electronics Engineering, Dhaka University, Amar Ekushey Hall, Dhaka, Bangladesh, Tel: 8801687478820; E-mail: sabbir1388@gmail.com

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	Volume of NH_2-CS-NH_2	Volume of $Zn(CH_3COO)_2.2H_2O$, (x)	Volume of $CdCl_2.H_2O$, (z)	Y= x/(x + z)	Label
Beaker 1	50 ml	10 ml	40 ml	0.2	A
Beaker 2	50 ml	20 ml	30 ml	0.4	B
Beaker 3	50 ml	30 ml	20 ml	0.6	C
Beaker 4	50 ml	40 ml	10 ml	0.8	D

Table 1: Experimental solutions with different volume proportion.

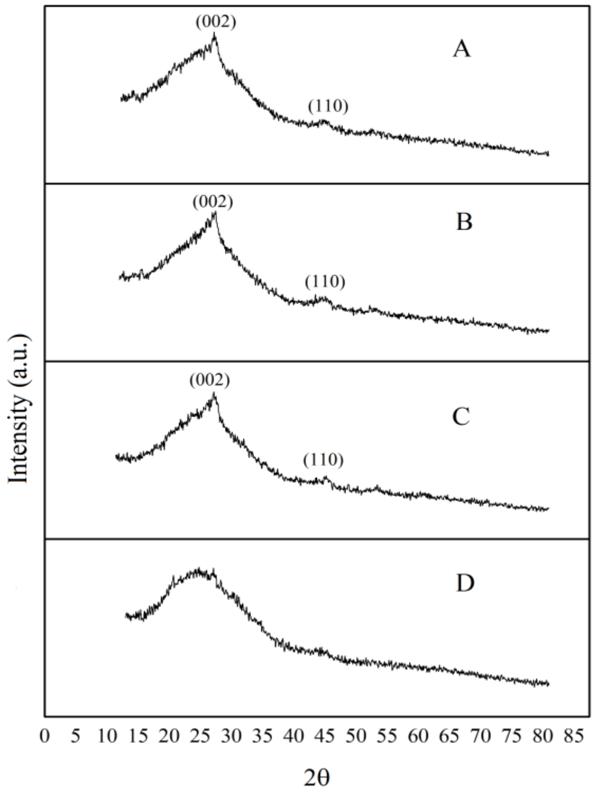

Figure 1: XRD images of CdZnS thin films.

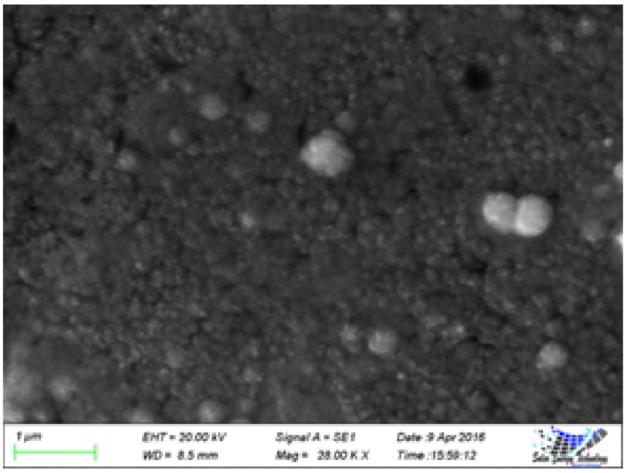

Figure 2: SEM image of CdZnS thin film.

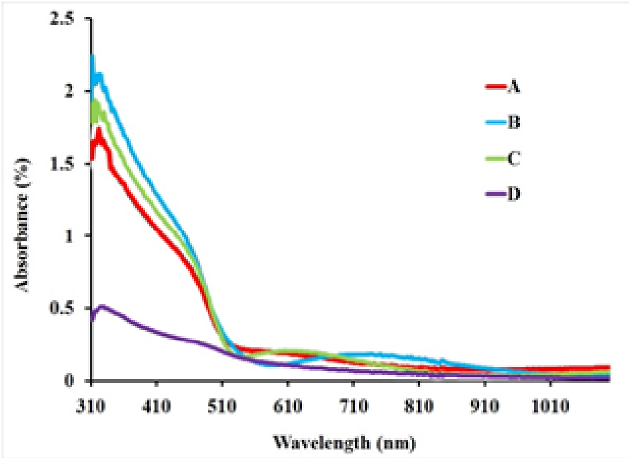

Figure 3: Absorbance vs. wavelength graph.

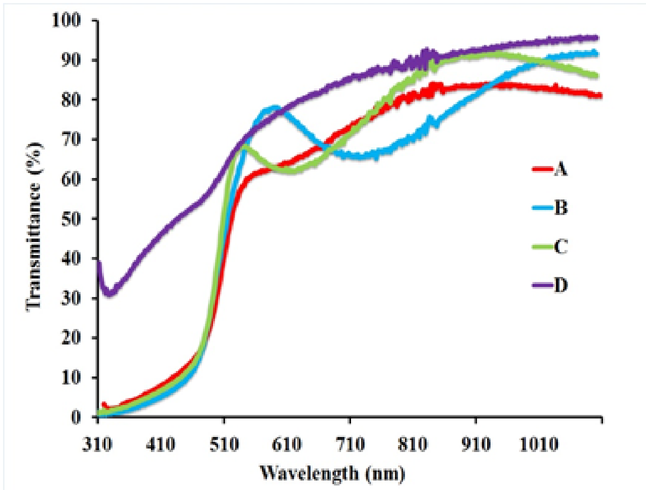

Figure 4: Transmittance vs. wavelength graph.

thin films. Figure 2 shows highly magnified image of the film obtained by SEM. Figures 3 and 4 are the absorbance and transmittance graph constructed from the data obtained by UH4150 spectrophotometer. Average transmittance of the films exceeds above 70% for wavelength of 500 nm and above. Film with Y=0.8 gave the best result with the transmittance reaching to 80% at just 600 nm wavelength and exceeding 85% barrier at around 700 nm wavelength (Figure 4). The direct optical band gaps (Eg) of the CdZnS thin films were found to be in the range of 2.83-2.93 eV. Results obtained by four point probe and Hall Effect measurement is presented in Table 2.

Discussion

XRD was carried out to investigate the crystalline properties of the films grown. Figure 1 shows that the films labelled as A, B and C show strong peaks in (002) and (110) planes of reflections. These are the characteristic peaks of CdZnS crystal having wurtzite structure (JCPDS card no: 40-0835) which confirms the formation of CdZnS crystal. XRD pattern of film D shows a broad maxima instead of a sharp peak

Label	Thickness (nm)	Bandgap (eV)	Resistance (Ω)	Sheet resistance (Ω/cm^2)	Mobility (cm^2/Vs)
A	165	2.83	53.9	236	411.8
B	150	2.91	55	241	37.79
C	270	2.93	56.8	249	10.75
D	71	2.92	63.9	280	8.499

Table 2: Optical and electrical properties of CdZnS thin films.

in the (002) plane. This confirms that this film is amorphous in nature. This amorphous nature is due to the large proportion of Zn-content present in the film. From these XRD data it can be said that the amount of Zn-content has a significant impact on the quality of crystal that is produced. CdZnS thin films crystallinity decreases as the Zn-content increases.

SEM image in Figure 2 shows that the film is very uniform in nature. But, there are some large sized particles present in the film which confirms the formation of secondary compounds during the deposition process.

The optical bandgap was estimated from the absorbance data (Figure 3) obtained by UV-visible spectrometry. Absorbance (A) is related to the absorption coefficient (α) and thickness (d) of the film by $\alpha h\nu = B\ (h\nu - E_g)^r$. The energy gap was estimated using the Tauc equation [15], $\alpha h\nu = B\ (h\nu - E_g)^r$ assuming a direct allowed transition between valence band and conduction band where, B is constant, $h\nu$ is the incident photon energy and r is constant (for direct transition r equals 1/2, and for indirect transition equals [2]. From the plot of $(\alpha h\nu)^2$ vs $h\nu$, E_g was estimated by extrapolating the straight line portion of the spectrum to $\alpha h\nu$=0. These Tauc plots are obtained from the absorbance spectra measured by the UV-visible spectrometry in the 300-1100 nm wavelength as shown in Figure 3. Estimated bandgaps show an increase in value as the Zn-content in the film is gradually increased.

Samples resistance and samples sheet resistance were measured by the four point probe technique. These two data were found to increase in their magnitude as the value of Y were increased. This is due to the increased addition of Zn to the film as Y increases. The conductivity and mobility of the film were measured by Hall Effect measurement technique. Data in Table 2 shows that increased proportion of Zn-content decreases the mobility of electrons in the film.

Conclusions

In summary, we developed CdZnS thin films in four different conditions to clearly illustrate the effect of Zn-content and to achieve higher transmittance of the films for photovoltaic application. X-ray diffraction confirmed the formation of transparent yellow colored hexagonal crystal structured CdZnS films. The crystallinity of the films was found to decrease with increasing Zn-content. The films showed an average transmittance of 70% in 500-700 nm range. Transmittance reached in between 85-90% for wavelength of 700 nm and above. It was found that changes in Zn-content changes the optoelectronic properties of the film. Resistivities of the samples were found to increase with increasing Zn-content. Optical band gap increased gradually from 2.83 eV to 2.93 eV as the Zn content was increased. All these results confirm the effect of Zn-content in CdZnS films. The improved transmittance of the films also confirms that the described preparation method is suitable for the deposition of CdZnS thin films for solar cell application.

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