Zinc Doped of CdS Layers Deposited by Chemical Bath Deposition Method

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Abstract: The chemical bath technique (CBD) uses to deposit the thin layers of CdZnS. we study the properties of CdxZn1-xS layers deposited by chemical bath (CBD) as surface morphology, structural, optical and chemical properties were studied by spectrophotometer SEM, XRD, EDAX and UV-visible. The transmittance is 80% in the visible region from 300 nm to 800 nm; the crystalline structure is hexagonal and cubic, the grain size is between 9.95 and 25.82 nm.

1 INTRODUCTION

In photovoltaic the material most used is silicon. But the silicon is not the ideal material for solar cells based on thin films because of their low absorption coefficient and a high cost of the product it. For these reasons, there are many researchers on other materials in order to replace the silicon. Among these materials, the Semiconductors groups II-VI are the best candidates. The use of semiconductor thin films have generated much interest in the development of various applications in various electronic and optoelectronic devices (T. Gruszecki, 1993), (D. Xia, 2011). The importance of technology-based thin film devices is mainly due to their low production costs. The Cd_xZn_{1-x}S is a group II-VI important semiconductor material (T.D. Dzhafarov, 2006, T. Prem Kumar, 2011), Cd_xZn_{1-x}S alloy compounds have attracted technological interest because their energy gap can be adjusted and network parameters can be modified (Ng. Gaewdang, 2005, A. Mukherjee, 2015). Cd_xZn_{1-x}S ternaries can form a continuous series of solid solutions, allowing variation of the band gap of Cd_xZn_{1-x}S from 2.43 eV for CdS to 3.7 eV for ZnS by adjusting the composition. CdZnS thin films were deposited by a

variety of techniques, for example, Chemical Bath Deposition (CBD)] (R. Mariappan, 2011, P.B. Bagdare, 2010), Spray Pyrolysis (Y. Ravi Prakash, 2010, M. Glatettin, 2010), Successive Ion Layer Adsorption and Reaction (SILAR) (G. Laukaitish, 2000), vacuum evaporation (D. Patidar, 2008, P. Kumar, 2004), the method Dip Coating (M. Abdel Rafea, 2009) and the screen printing technique (V. Kumar, 2012). Chemical deposition processes are the low-cost process. The layers obtained found to have comparable quality to those obtained by the more classy and expensive physical deposition methods. The Chemical Bath Deposition is an evolution of the process by controlled precipitation from solution. This process has recently been developed for the deposition of thin layers of the metal chalcogenide. CBD method attracts attention today because they do not require sophisticated and expensive equipment (vacuum systems): simple hot plates with a magnetic stirrer are required. In this work have been synthesized and studies the proprieties (optics, morphological and chemical composition) of CdZnS thin films obtained by Bain chemical deposition, to replace the CdS in the solar cell.

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2 EXPERIMENTAL

CdCl₂, Zn ((C₂H₃O₂)₂. 2H₂O) and NH₂-CS-NH₂ were used as ion source materials for Cd^{2+} , Zn^{2+} and S^2 , respectively. The experimental detail located in reference (R. Zellagui, 2019). The films were prepared under continuous stirring. The deposition time was 30 minutes. The deposited films were cleaned with de-ionized water and alcohol. Cleaning was necessary to remove the surface impurities and minimize the particle agglomeration. Deposited films were dried with N_2 gas. As deposited, $Cd_xZn_{1-x}S$ thin films were in golden vellow color. Annealing used furnace vacuum at temperature was 500 ° C for 1 hour. The performance of the transmittance of visible light of the sample was measured using a Shimadzu UV-1800 spectrophotometer. The surface morphology of the film was carried out using scanning electron microscopy (SEM) model JEOL JSM-6610LA. The crystal structure of the samples was characterized by an X-ray diffractometer Bruker with a Cu-K α radiation with wavelength (1.54 Å) and the Raman spectra were recorded with a Bruker SENTERRA R200L spectrometer

3 RESULTS AND DISCUSSION

3.1 Morphological Proprieties

Fig. 1 shows the SEM surface images of $Cd_xZn_{1-x}S$ thin films of composition x=0.7, 0.5, 0.1, respectively. As the composition (x) increases Zn is more incorporated into CdS films. Which are indicated by XRD as well as SEM (S.V. Borse, 2007). The CdZnS layer constituted of a dense layer of small crystallites and few large particles are embedding in the surface. These particles are quite likely $Cd_xZn_{1-x}S$ colloidal particles formed on the substrate during film growth. The shape of particle is changing with increases of Zn concentration.





Fig. 1 Typical SEM images of nanostructured $Cd_xZn_{1-x}S$ thin films (a=Cd_{0.1}Zn_{0.9}S, b= Cd_{0.5}Zn_{0.5}S, c= Cd_{0.7}Zn_{0.3}S) annealed at 500 °C.

3.2 Optical Properties

The optical transmission of CdZnS thin films with different concentrations is using the Spectrophotometer UV-visible (Shimadzu UV-1800). We observe that the transmittance of our samples is varied between 60 and 80% in visible region this variation due to the decrease in Zinc concentration. Whereas in the region <450 nm fundamental absorption therefore, our thin films possess transparency performance in the 450-800 nm region, the latter gives them great importance in solar cells as a buffer layer.



Fig. 2 Transmission spectra of $Cd_xZn_{1-x}S$ thin films.

The optical band gap Eg was obtained by extrapolating the linear portion of the plot $(\alpha hv)^2$ versus (hv) to $\alpha = 0$, according to the following equation (Y. Bakha, 2011):

$$\alpha = A (hv - Eg)^n \tag{1}$$

Where hv is the photon energy, Eg is the band gap, A is the edge parameter and n = 1/2 for direct gap material.

The values of optical band gap Eg of thin films $(Cd_{0.7}Zn_{0.3}S, Cd_{0.5}Zn_{0.5}S \text{ and } Cd_{0.1}Zn_{0.9}S)$ are (3.5, 3.61 and 3.8 eV) respectively, we find that the gap energies of our thin layers are closer to that of ZnS (K. Nagamani, 2012, T. Ben Nasr 2006).





Fig. 3 Extrapolations of E_g for $Cd_xZn_{1-x}S$ thin films.

3.3 Chemical Composition

Quantitative analysis by EDX mines layers of CdZnS was carrying out to investigate the stoichiometry. The results are present Fig.4, which confirms the presence of Cd, Zn and S, with atomic percentages of Cd / Zn / S: 19.36 /60.43 /20.20, 42.69/19.08/38.23 and 40.41/23.35/36.23 for three concentrations of Cd_{0.1}Zn_{0.9}S, Cd_{0.7}Zn_{0.3}S, and Cd_{0.5}Zn_{0.5}S (A. Abdolahzadeh Ziabari, 2013), (] S.D. Chavhan, 2008).





Fig. 4 EDX spectra for CdZnS thin films (a = $Cd_{0.1}Zn_{0.9}S$, b= $Cd_{0.7}Zn_{0.3}S$, c= $Cd_{0.5}Zn_{0.5}S$)

3.4 Structural Proprieties

X-ray diffraction (XRD) spectra give information on the nature of structure and the composition of a thin film. These XRD diagrams confirm the formation and composition of the alloys of the ternary system $Cd_xZn_{1-x}S$ with x = (0.1, 0.5, 0.7) are present in FIG. 5 Peaks: (100), (002), (101), (110), (103), (200) and (201) correspond to the hexagonal structure of the thin films of Cd_{0.7}Zn_{0.3}S and Cd_{0.5}Zn_{0.5}S (ASTM JCPDS File No. 491302 and 241136). The peak (002) is the most intense for Cd_{0.7}Zn_{0.3}S and Cd_{0.5}Zn_{0.5}S. But for $Cd_{0.1}Zn_{0.9}S$ the peaks are (111), (200), (210), (211), (300), (222), (321) and (400), the most intense peak is (200) correspond to the cubic structure (JCPDS file No. 079-6257 and 6259 of ASTM). The average size of the crystallites of CdZnS estimated according to the formula of Debye-Scherer's [23].

$$D = 0.9\lambda / \left(\Delta \left(2\theta \right) \cos \theta \right) \tag{2}$$

Where D is the crystallite size, $\lambda = 0.154$ nm the mean wavelength of Cu K α radiation and $\beta = (\Delta 2\theta)$ is the full-width half maximum (FWHM) of Bragg peak observed at Bragg angle θ (rad), K = 0.9, the values of D obtained. The grain size values, of $Cd_xZn_{1-x}S$ thin layers deposited at bath temperature $80 \pm 5 \circ C$ and annealed at 500 ° C are shown in Table 1. From the table it can be seen that the size of the crystallites increases with increasing zinc compositions (x) (R. Mariappan, 2011).

The lattice parameter values were calculated using the formula (3) and (4):

$$1/d^{2} = 4/3 \left((h^{2} + hk + k^{2})/a^{2} \right) + l^{2}/c^{2}$$
(3)

$$1/d^2 = (h^2 + k^2 + l^2)/a^2 \tag{4}$$

Moreover, the obtained values are compiled in Table 1 (D. Patidar, 2008), the lattice parameter is decreased when the zinc concentration increases, when the zinc concentration is greater than 0.5 M the crystal structure changes from hexagonal to cubic.

Tab.1 XRD results of CdZnS thin films.





Fig. 5 XRD pattern of $Cd_xZn_{1-x}S$ thin films.

4 CONCLUSIONS

Synthesis CdZnS thin films by chemical bath deposition (CBD) were easy and feasible for deposition on large-area glass substrates. The study of the characterizations showed that the morphology of the surface and the transmittance are modified with respect to the zinc concentration. The energy of the interval is of the order of 3.5 to 3.8 eV. The crystalline structure is hexagonal for $(Cd_{0.7}Zn_{0.3}S)$ and $Cd_{0.5}Zn_{0.5}S$ and cubic for $Cd_{0.1}Zn_{0.9}S$. and the grain size is between 9.95 and 25 nm.

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