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DEVELOPMENT OF LOW COST AND LARGE AREA NOVEL CHEMICAL SYNTHESIS OF CHALCOGENIDE THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

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ABSTRACT

We deposit CdS/ZnS chalcogenide semiconductor thin films on different substrates by Chemical Bath Deposition Method. We record X-ray diffraction pattern and SEM of the developed samples. It is found that, the average grain size of the CdS/ZnS in the film is 08 to 113 nm. The physical conditions were kept identical while growing all the samples. It is also observed that energy band structure and band gaps get changed because of the grain size of the sample in the films. We predict that the difference in grain size of the CdS/ZnS in the thin films may be because of the binding energy of Cadmium and Zinc in the molecules of CdSO₄ and Zn (CH₃COO)₂. The investigation of the method of synthesis on the grain size and the effect of grain size on the properties of semiconductor is under consideration.

Key words: Low cost, Chemical synthesis, Chalcogenide, Thin film, Photovoltaic.

INTRODUCTION

Zinc and cadmium sulfide are compound semiconductors with a wide range of potential applications. The CdS / ZnS is an excellent material used with the semiconductor cadmium telluride to fabricate solar cells given its optimal band gap energy (2.42 eV) for optical windows, while great importance in the optoelectronic applications and a diverse range of applications for thin films of this semiconductor including as waveguides, heterojunction devices and in thin-film electroluminescent displays in which it is the most commonly used host material. Applications in opt electric methods or photovoltaic devices is another area receiving attention , In CdS based solar cells, the use of wider band gap materials such as ZnS or CdZnS could lead to decreases in window absorption losses and improvements in the short circuit current of the cells.

In this work we developed the ZnS and CdS semiconductor thin films having a nanometer grain size by using Chemical Bath Deposition (CBD) Technique. The (CBD) is one of the most convenient, reliable, simplest, inexpensive method and useful for large area industrial applications as well as preparation of thin

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film at close to room temperatures. The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. The technique offers many advantages over the more established vapor phase synthetic routes to semiconductor materials, such as CVD, MBE and spray pyrolysis. Factors such as control of film thickness and deposition rate by varying the solution pH, temperature and reagent concentration are allied with the ability of CBD to coat large areas, in a reproducible and low cost process. Another advantage of CBD method with respect to other methods is that the films can be deposited on different kinds, shapes and sizes of substrates^{1,2}.

EXPERIMENTAL

Thin films of CdS / ZnS were deposited from a solution of analytical grade CdSO₄ (Cadmium Sulphate) / Zn(CH₃COO)₂ (Zinc Acetate) a Cd⁺⁺ / Zn⁺⁺ ion source and Thiourea as a S⁻⁻ ion source in an alkaline solution of Ammonia. Commercial glass slides, used as substrates, were cleaned in acetone and methanol ultrasonically, and finally, again washed with methanol ultrasonically before use. After cleaning the glass slides were kept vertically in a closed beaker with the help of a special holder which is attached to AC Motor having a constant speed of 60 r.p.m. After the deposition, the CdS / ZnS films were washed with methanol ultrasonically to remove the loosely adhered CdS / ZnS particles on the film and finally dried in air. The same procedure is repeated for different time durations^{3,4}.

The crystallographic structure of films was analyzed with a diffractometer (XPERT-PRO) by using Cu-K α lines (λ = 1.54 Å). The average grain size in the deposited films was obtained from a Debye-Scherrer's formula. The SEM studies were performed with a PHILIPS 515 electron microscope. Also we were changing the different parameters such as Time, Molarities, pH and Temperature and note the effects on deposition rate of thin films.

RESULTS AND DISCUSSION

Film structure studies

The as-grown CdS thin films were characterized by the XRD technique scanned in the 2θ range of $0-60^{\circ}$. The diffractograms were obtained for the films grown on the amorphous glass substrates (Fig. 1).



Fig. 1: X-Ray diffraction pattern of as deposited CdS thin films on glass substrate

The diffractograms depict that the deposits are polycrystalline in nature. It is seen that the plane (1 1 1) of CdS appears with higher peak intensity in all the diffractograms. A well matching of the observed and the standard d-values from JCPDS data card [6-7] confirms the formation of compound CdS with mixed

cubic and Hexagonal crystal structure. The calculated values of lattice constant with cubic crystal structure are found to be a = b = c = 5.8200 Å agreeing well with the standard values CdS [7]. The grain size was calculated for all cases for the reflections from the C (111) plane by using the well known Debye-Scherrer formula,

$$D = 0.9\lambda/\beta\cos\theta \qquad \dots (1)$$

where D is the particle size, β is the full width broadening of the diffraction line measured at half of its maximum intensity in radians (FWHM), λ is the X-ray wavelength(1.5406 Å) and θ is Bragg diffracting angle. From particle size analysis it is clear that the films are nanocrystalline in nature. The grain sizes were found to be within the range of 11 to 121 nm^{6,7}.

Surface morphology studies

The surface morphology of deposited CdS thin films was investigated by SEM at different magnifications as shown in Fig.2.



Fig. 2: Scanning electron micrograph of as deposited CdS thin film at different resolutions magnification

The deposits are compact, pinhole free with spherical grains from few nanometers up to clusters of 157 nm and the films are well covered on the substrate. From the figure, it is observe that the small nanosized grains engaged in a fibrous- like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdS thin films. The average grain size of the CdS nanoparticles is about 130 nm. This result is in consistent with results obtained from X ray diffraction studies¹²⁻¹⁴.

Optical absorption studies

The optical absorption spectrum of the deposited CdS thin films on glass substrate was studied in wavelength range 200 to 800 nm. The nature of the transition involved (direct or indirect) during the absorption process was determined by studying the dependence of the absorption coefficient α , on photon energy hu as¹⁵.

$$\alpha h \upsilon = A (h \upsilon - Eg)^n \qquad \dots (2)$$

Where A is the constant, Eg is the bandgap energy, hv is the photon energy, $n = \frac{1}{2}$ or 2 for direct or indirect transition. The value of absorption coefficient is found to be of the order of 10^4 cm⁻¹. The optical data was further analyzed to determine the nature of transition that takes place in CdS thin film. The plots of $(\alpha hv)^2$ versus hv are shown in the Fig. 3.



Fig. 3: Plots of $(\alpha hv)^2$ versus hv of as deposited CdS thin films on glass substrates.

The straight line nature of the graphs supports the direct bandgap nature of the semiconductor. The straight-line portion was extrapolated to the energy axis at $\alpha = 0$, to obtain the band gap of CdS thin films. The direct optical band gap of the CdS film estimated to be 2.42 eV agrees well with the reported value for CdS material¹⁵.

CONCLUSION

The chalcogenides semiconductor thin films of CdS and ZnS have been successfully deposited by simple and inexpensive Chemical Bath Deposition Technique. Polycrystalline nature of as deposited thin films was predicted from X-ray diffraction studies. Scanning electron microscopy studies revealed uniform deposition with the average grain size of 113 nm. The UV absorption studies on films clearly show an increase in band gap with reduction in particle size as compared to bulk materials, which supports the formation of nanocrystallites in these films. The optical band gap was found to be 2.42 eV with direct allowed transition.

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