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Studies on growth and characterization of CdTe thin films deposited by chemical bath deposition technique

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ABSTRACT

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The CdTe thin films were prepared by chemical bath deposition technique, also known as solution growth technique using commercial glass as substrate at 358K bath temperature using cadmium acetate andtellurium dioxide. Characterization was done by X-ray diffraction method, the scanning electron microscope (SEM) micrographs, optical spectrophotometer and the quantitative analysis using the energy dispersive X-ray analysis (EDAX). X-ray diffraction study indicates the hexagonal structure. The band gap calculated from optical spectra was found to be 1.41eV. The EDAX peaks shows the presence of Telluriumand Cadmiumin the as-deposited thin film of CdTe.

Keywords: Nanocrystalline thin films, Chemical bath deposition, X-Ray diffraction, Scanning electron microscopy.

INTRODUCTION

The II-VI group semiconductor compounds (CdSe, ZnSe, CdS, CdTe, etc)are of great importance because of their applications in optoelectronics, solar cells, integrated and electro optic devices. Chemically deposited CdTe thin films have received immense attraction due its applications in photovoltaic devices, microelectronics, switching devices, thin film transistors, etc.[1-4]. CdTe is a direct band semiconductor having a band gap in the range of 1.4 - 1.5 eV at room temperature [5-7] which is ideal for solar cell radiation. It possesses properties such as high resistivity and high absorption ($> 10^4$ cm⁻¹) for the visible solar spectrum[8-9]. Thin film solar cells of CdTe semiconductor materials having power conversion efficiency of 17.3% have been reported. The physical properties of the deposited thin film depends on the technique used to deposit the film. In this regard, many fabrication techniques have been attempted to grow CdTe thin films including pulsed laser deposition [10], physical vapour deposition[11], hot well epitaxy[12], RF sputtering[13], successive ionic adsorption and reaction method[14], chemical bath deposition (CBD) technique is one of the simplest and the most economical technique used for the preparation of the thin films. It is uniquely suitable for deposition of a uniform film over large substrates having complex geometries. The substrates need not be conductive or have high melting point or be combustion resistant. The properties of the thin films deposited using CBD method depends on various parameters such as the

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concentration of the chemical bath, the pH of the solution, deposition time, temperature etc. The chemical bath deposition technique is well suited to prepare thin films of chalcogenide semiconductors for solar cell related applications.

There have been few reports in the literature on the preparation of CdTe thin films using the CBD technique [17]. Padam and Malhotra reported deposition of CdTe thin films on glass substrate and ITO coated glass, silicon wafer and micausing CdCl₂ as cadmium source and TeO₂ as Tellurium source in alkaline medium along with triethanaloamine (TEA) as complexing agent and hydrazine hydrate (HH) as a reducing agent[18]. Deivanayaki et.al deposited the CdTe thin film on glass substrate at 358K using cadmium acetate and tellurium dioxide. The films were annealed at 623K, 673K and 723K[1]. Klochko et.al deposited the CdTe thin film using cadmium sulphate and tellurium dioxide in acidic medium [19]. Garadkar et.al deposited CdTe thin films using cadmium sulphate as a source of Cd²⁺ ions and sodium tellurosulphite as a source for Te²⁻ using the CBD method[20]. It is observed that most of the deposition was carried out at temperatures ranging from 353K to 371K.

In this paper, an attempt has been made to prepare CdTe thin films on glass substrate by optimizing the concentration of the complexing agent, deposition time, temperature, pH and concentration of cadmium and tellurium salts by using the CBD technique at 358K and to investigate the optical, structural and electrical properties of the as-deposited film.

MATERIALS AND METHODS

2.1. Substrate cleaning:

Glass slides of dimension 76mm X 26mm X 2mm were used as substrate for deposition of thin film. Initially the glass slides were cleaned thoroughly with distilled water and were then ultrasonically cleaned for 10 min. Then it was degreased using chromic acid and then rinsed with deionized water.

2.2. CdTe film formation on the substrate:

CdTe thin films were deposited on commercially available glass plate of 2mm thickness by using the CBD technique. The cleaned glass slides were placed vertically on the walls of the beaker containing the deposition mixture for the deposition of the film.

Chemical bath constituted 0.8M solution of cadmium acetate ,[Cd (CH₃OO)₂, 2H₂O]which was used as source of cadmium and 0.07M solution of tellurium dioxide [TeO₂] as a source for tellurium. Triethanoloamine (TEA) was used as a complexing agent to form Cd[TEA]²⁺ for controlling growth rate. Hydrazine hydrate [H₂N-NH₂.H₂O] was used as a reducing agent for tellurium. The role of hydrazine hydrate is to reduce Te⁴⁺ ions in TeO₂ to Te²⁻

Double distilled water was used to dissolve cadmium acetate and magnetically stirred. To this solution 25ml of TEA as complexing agent and 8ml of hydrazine hydrate was added. 25% of ammonia was added to this solution till the pH is 12.5. 0.07M TeO₂ dissolved in hot diluted sulphuric acid is then added to the solution of cadmium acetate and then magnetically stirred for 10minutes. The cleaned glass substrates were immersed into beakers containing the deposition solution. In order to control the rate of film growth on the glass substrates, the bath temperature was kept constant at 358K. At the end of deposition process, all the deposited substrates were removed from the chemical bath after 60min of deposition time. The substrates were washed with deionized water to remove the loosely adhered CdTe nanoparticles on the film and then dried. The overall reaction is as follows

 $[Cd(TEA)_n]^{2+} + Te^{2-} + 2OH^- = CdTe + n(TEA) + H_2O$

3. Characterization of CdTe thin film:

The CdTe film thickness was determined by gravimetric weight difference method. For this, a sensitive microbalance was utilized and film density was assumed as the bulk density of CdTe (5.85 g cm⁻³). The X-ray diffraction studies were carried out in the range of the scanning angle $0-80^{\circ}$ with CuK-radiation ($\lambda = 1.5406$ Å) using PW-1710 diffractometer. Optical characterization was done by recording absorption spectra of the sample using a double beam spectrophotometer (Hitachi-220) in the wavelength range 350-850nm. The electrical resistivity of the film was measured using a d.c. two probe method in the temperature range 323–473K. A brass block was used as a sample holder. A chromel–alumel thermocouple was used to measure the temperature difference. The area of the film was defined (0.25 cm²) and silver paste was applied to ensure good ohmic contacts to the film. The

microstructure and surface morphology was analyzed by taking Scanning Electron micrograph using SEM (model S-2400 Hitachi) equipped with an EDAX-DX-4 analyzer to measure qualitatively the sample stoichiometry.

RESULTS AND DISCUSSION

The as-deposited CdTe thin film was grey in colour and had a shiny finishing.

4.1. Structural Studies:

The X-ray diffractogram of the as-deposited CdTe film reveals the crystal structure of the film deposited by CBD technique. The XRD peak shows that CdTe is nanocrystalline with a hexagonal structure with peaks at $2\theta = 24.47$, 34.93 and 53.16 with the orientations (1 0 1), (0 1 3) and (0 0 6) respectively. The observed values are compared with JCPDS data 82474 and are found to in good agreement with standard values. The lattice parameters are found to be a = 4.29° A and c = 10.23° A.



Fig.1- X-ray diffraction pattern of CdTe thin film (358K).

Using FWHM data and Debye-Scherrer's relation, the average crystallite size of the material was calculated from the XRD data

$$D = \frac{0.94\lambda}{\beta cos\theta}$$

Where $\lambda = 1.5406 \text{ A}^{\circ}$ for CuK α , β is the full width at half maximum (FWHM) of the peak and θ is the diffraction/Bragg's angle. The average crystallite size of the as deposited CdTe thin film was found to be 15.29nm at optimized preparative parameter.

4.2. Surface Morphological Studies:

The SEM micrographs of the CdTe thin film prepared from CBD technique on a glass substrate at 358K is shown in fig.2. The micrographs reveals that the film is well adherent, homogeneous and well covered to the substrate surface without any cracks and pinholes.



Fig.2- The SEM micrographs of CdTe film grown on glass substrate at 358K.

The quantitative analysis of the films grown at room temperature was carried out by using the Energy Dispersive X-ray analysis (EDAX). The EDAX was recorded in the energy region 0-14KeV.The EDAX micrograph gives quantitative analysis of Cd and Te in the as-deposited CdTe thin film. From EDAX analysis, it was found that all the films were nearly stoichiometric.

4.3. Optical absorption studies:

The variation of optical density with wavelength was analyzed to find out the nature of transition involved and the optical band gap, using the relation

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$$

where A is a constant, α the absorption coefficient and n is equal to $\frac{1}{2}$ for direct band gap semiconductors. The energy gap E_g could be obtained from the intercept of $(\alpha hv)^2$ versus hv for direct allowed transitions. For direct allowed transitions, $n = \frac{1}{2}$. The optical properties of the CdTe films were measured by using UV-VIS-spectrophotometer at room temperature in the wavelength range of 300-1000nm.



Fig.3- Plot of $(\alpha hv)^2$ versus hv for CdTe thin film

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The plot of $(\alpha hv)^2$ versus hv is shown in Fig.3 for CdTe films having a thickness of 110 nm. Since the variation of $(\alpha hv)^2$ versus hv for CdTe thin film is a straight line indicating that the transition is direct. The energy gap was determined by extrapolating the straight line portion to the hv axis for zero absorption coefficient (α). The optical band gap was found to be 1.41eV for the as grown CdTe thin film having thickness 110nm.

4.4. Electrical resistivity measurement:

CdTe exhibits a semiconducting nature. It is possible to make CdTe n-type or p-type conductor by suitably doping it. Intrinsically, cadmium deficiency in CdTe material makes it an p-type semiconductor while deficiency of tellurium it becomes an n-type semiconductor. The electrical resistivity of the as-deposited CdTe film deposited on glass substrate was measured using a 2-probe method in air within the temperature region 323K-473K. Fig.4 shows the variation of logarithm of resistivity (log ρ) with reciprocal of temperature (1000/T). It is observed that resistivity decreases with increase in temperature, indicating semiconducting nature of CdTe film. The resistivity of the as-deposited CdTe film was found to be of the order of $10^3\Omega$ cm which is comparable to chemical deposited film reported by many researchers.



Fig. 4- Plot of log ρ Vs. (1000/T) for CdTe thin film

CONCLUSION

CdTe thin films were deposited on glass substrate by using the chemical bath deposition technique at room temperature. Grey color thin films with shiny surface were formed on the glass substrate. The XRD pattern confirms the hexagonal structure of CdTe film. The presence of Cd and Te elements were confirmed from the EDAX analysis. The SEM micrographs revealed the presence of spherical shaped clusters of size 20.75nm. From the optical analysis, the band gap energy was found to be 1.41eV. The electrical resistivity is of the order of $10^3\Omega$ cm.

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