Effect of pH on structural, optical, and morphological properties of ED-CdTe film

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Abstract. Cadmium telluride (CdTe) thin films have been deposited by electrodeposition (ED) technique on fluorine doped tin oxide (FTO) coated glass substrates using an aqueous electrolyte bath solution. The pH-value of the electrolyte solution is one of the most important deposition parameter that should be optimized to achieve high quality photoconductive material. The films have been deposited at different pH values ranging from 1.5 to 3. The structural, optical, and morphological properties of the samples were characterized using X-ray diffraction (XRD), UV–Visible (UV-Vis) spectroscopy, spectrofluorophotometer, scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX) techniques respectively. The XRD analysis shows that the ED-CdTe films possess the cubic crystalline structure and the diffraction peak intensity increased significantly after changing the pH values. The direct energy band gap \(E_g=1.44\) eV is obtained in optical absorption spectra. The SEM analysis shows very good morphological growth by changing the pH values and the film deposited with lower pH showed more intense PL emission peaks as compared to the other two films. CdTe film deposited at pH 1.5 will be better choice as an absorber layer of a CdTe/CdS solar cell.

1. Introduction

For the fabrication of solar cell devices, semiconductor thin films are the very promising and popular solar cell materials. Cadmium telluride (CdTe) is one of the most capable p-type semiconducting materials due to its suitable band-gap of 1.5 eV, high chemical stability, high absorption coefficient, and very good optical properties. The theoretical efficiency of CdTe thin film based solar photovoltaic (PV) devices with n-type cadmium sulfide (CdS) window layer 28%-30% and these cells have shown constant long-term performance. The first solar has introduced the new world record for CdTe photovoltaic (PV) solar cell efficiency of 22.1% and commercially available CdTe/CdS solar modules are available having an efficiency of 18.2% [1]. Here, the role of CdS window layer is to permit the energetic shorter wavelength photons to be transferred for the incidence at the hetero junction with minimum possible absorption loss. On the other hand, the CdTe absorber layer should absorb most of the solar radiation incident near the hetero-junction with minimum recombination losses. The fundamental requirement for the CdTe layer for good device efficiency is the minimization of bulk recombination and interface density [2]. CdTe have been deposited by variety of methods including chemical bath deposition (CBD) [3], electrodeposition (ED) [4], closed space sublimation (CSS) [5], radio frequency sputtering (RF) [6], laser ablation [7] etc. Electrodeposited CdTe thin film layer is the best absorber layer for polycrystalline CdTe/CdS thin film solar cell [8]. Additionally, ED is quite easy, simple and inexpensive technique. This method provides good control over preparatory conditions such as stirring rate of the solution,
deposition time, growth temperature, concentration of the solution, and pH of the electrolyte. In the present work, CdTe thin films have been deposited on FTO substrate using 2-electrode ED technique at different pH of electrolyte bath ranging from 1.5 to 3.5. The main purpose of this work is to determine the optimum pH where the PV activity of CdTe layers can be achieved for development in thin film solar cells.

2. Materials and methods
CdTe electrolyte solution is prepared with cadmium sulphate (CdSO₄), tellurium dioxide (TeO₂), and sulphuric acid (H₂SO₄). Here, very low concentration of Te (~1.0–5.0mM) and high concentration of Cd (0.5–2.0M) are maintained. For this, 1000 ppm of cadmium chloride (CdCl₂) is added to the aqueous solution. Three different CdTe solutions are prepared at different pH values 1.5, 2.5, and 3.5. The solution is heated at 65°C for 10 min and meanwhile the solution was stirred constantly at 300 rpm using a hotplate magnetic stirrer. A saturated graphite electrode and a transparent glass/Fluorine doped tin oxide (FTO) having sheet resistance (7Ω/square) are employed here as anode and cathode, respectively. CdTe films were washed by distilled water after the completion of deposition and dried in air. With the help of a hot air oven, all three films were then annealed for 10 min at 150°C. Resulting samples were analyzed to reveal the difference in their structural, optical, and morphological properties in accordance with the different pH values.

Optical absorption measurements have been performed using the Shimadzu make UV-1800 spectrophotometer and the band-gap energy values of ED-CdTe films are determined by extrapolating the linear portion of the (αhv)² vs. hv plot. The surface morphological characteristics of the FTO/CdTe layer are studied using the scanning electron microscope (Zeiss EVO 18). The structural properties of the samples have been studied by PANalytical X’pert multifunctional powder X-ray diffractometer using Cu-Kα radiation (λ=1.54 Å) in the scanning range from 20° to 90°. Luminescence behaviour of the films is studied using spectrofluorophotometer (Shimadzu made) instrument. The film deposition process is governed by the following chemical reactions [9]:

\[
\begin{align*}
\text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^- & \rightarrow \text{Te} + 2\text{H}_2\text{O} \\
\text{Cd}^{2+} + 2\text{e}^- & \rightarrow \text{Cd} \\
\text{HTeO}_2^+ + \text{Cd}^{2+} + 3\text{H}^+ + 6\text{e}^- & \rightarrow \text{CdTe} + 2\text{H}_2\text{O}
\end{align*}
\]

3. Results and Discussions
3.1 UV-Visible (UV-Vis) studies
Information related to optical properties such as band-gap energy (E_g), transmission and absorption behaviour of deposited films is very important for the fabrication of a good quality PV device. Fig. 1 shows the graph plotted between (αhv)² and photon energy (hv). The band-gap values for CdTe films deposited at pH values of 1.5, 2.5, and 3.5 were estimated from intercepts on hv axis, which are obtained as 1.44 eV, 1.48 eV, and 1.53 eV, respectively. From this graph it can be noticed that when pH value of electrolyte solution increases the band-gap of the CdTe film increases. The above results are close to the band-gap value of CdTe documented in the literature [10-11].
3.2 Photoluminescence (PL) studies

The emission of light caused by the irradiation of a material with other light is known as PL. Fig. 2 shows the PL spectra of ED-CdTe layers deposited at different pH values. In this PL study, the source of excitation was laser beam (He-Ne) of wavelength 632 nm (1.96 eV). PL band observed at 800 nm ($E_g = 1.55$ eV) is related to band to band transition. The weak PL band obtained at 840 nm ($E_g = 1.47$ eV) is related to the band to band transition or recombination of holes and electrons through surface/defect states. These findings are in good agreements with the the previous studies [12]. Both of these PL bands are obtained for the films deposited at pH 1.5 and 2.5, but the intensity of second PL band situated at 840 is very low for the film deposited at pH 2.5. Also, only first PL band (800nm) is seen in the PL spectra of CdTe film deposited at pH 3.5. This result indicates that pH of 1.5 is suitable for growing stoichiometric CdTe layer to be used as absorber layer in a solar cell.

Figure 1. Tauc’s plot of ED-CdTe films deposited at different pH values.

Figure 2. PL spectra of ED-CdTe films deposited at different pH values.
3.3 Scanning electron microscopy (SEM) studies
In the development of thin film solar cells, fundamental knowledge about the surface morphology of constituting layers is very important. SEM is a microscope that produces images of a sample by scanning the surface with focused beam of electrons. SEM images are recorded using 20KV electron beam voltage and 20000 magnifications (Fig. 3). Fig. 3(a) is the SEM image of FTO/CdTe layer having pH value of 1.5. The grains exhibit large in size and cauliflower like structure. Fig. 3(b) and (c) are the SEM images of CdTe layer having pH value of 2.5 and 3.5, respectively. It shows the agglomeration of crystalline consisting of many smaller size grains and these films looked somewhat blurred as their morphology got disturbed by increasing pH concentration [13]. Another study found that the better morphological behavior has been obtained for the film deposited at Low pH as it helps to prevent the formation of phases of cadmium hydroxide and improves the solubility of Tellurium in electrolyte solution [14]. Also, the rate of deposition of CdTe layer became slow at higher pH value due to the less availability of H+ ions [15] thus the film deposited at low pH values are more preferable choice for PV application than the film deposited on higher pH value.

![Figure 3. SEM micrograph of ED-CdTe films deposited at different pH values.](image)

3.4 X-Ray Diffraction (XRD) studies
XRD is a process in which atoms of a crystal cause an interference pattern generated by incident X-ray beams depending upon the nature of their spacing. XRD is a popular characterization technique used for the identification of various issues related to the crystal structure of solids [16]. Fig.4 represents the XRD diffractograms of ED-CdTe films deposited at pH 1.5, 2.5 and 3.5. In the XRD pattern of CdTe film deposited at pH 1.5, four diffraction peaks (111), (002), (022) and (113) related to cubic phase situated at diffraction angles 24.4, 26.3, 37.9, and 46.0, respectively are seen. In the XRD pattern of CdTe film deposited at pH 2.5, all of the four peaks are observed but the intensities of the peaks decreased significantly. But, for the CdTe film deposited at pH 3.5 only two cubic phases (111) and
(113) were found. Some other peaks were found in the XRD images due to FTO substrates. It is clear from the above discussion that the CdTe film deposited at pH 1.5 has best crystallinity.

![XRD patterns of ED-CdTe films deposited at different pH values.](image)

**Figure 4.** XRD patterns of ED-CdTe films deposited at different pH values.

**4. Conclusions**

CdTe films have been successfully on FTO substrates at different pH value of the solutions using a 2-electrode ED setup. The influences of pH of aqueous electrolytes on structural, optical and morphological properties are studied. The results obtained from the optical absorption measurement show that FTO/CdTe layer deposited at pH=1.5, 2.5 and 3.5 have band-gap energy ($E_g$) 1.44 eV, 1.45 eV, and 1.52 eV, respectively. All three films are cubic crystalline in nature but the film deposited at pH 1.5 showed best crystallinity. The surface morphology of the films is found to improve for the lowest pH value 1.5. The film deposited with lower pH showed more intense PL emission peaks as compared to the other two films. The better material properties can be achieved at pH 1.5 and CdTe film deposited at pH 1.5 will be a good selection as an absorber layer of a CdTe/CdS solar cell.

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