

**CHEMICAL AND ELECTRON BEAM DEPOSITED
Cd Se_{1-x} Te_x THIN FILMS
AND THEIR APPLICATIONS IN PEC**

By
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CERTIFICATE

I am satisfied that the thesis entitled "Chemical and Electron Beam Deposited $\text{CdSe}_{1-x}\text{Te}_x$ Thin Films and Their Application in PEC" by J.P.Mangalhara is worthy of consideration for the award of the Degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him. The results contained in it have not been submitted in part or full to any other University or Institute for the award of any Degree/Diploma.

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ABSTRACT

The CdSe, CdTe and their solid solutions have interesting implications in thin film electro-optic devices and photoelectrochemical cells. The full range of solid solution can be obtained with 'tunable' band gap and lattice parameters. The present thesis is devoted to the deposition of thin films of CdSe and $\text{CdSe}_{1-x}\text{Te}_x$ ($0 \leq x \leq 1$); their characterization by studying structural, optical and electrical properties; and use of these films deposited on titanium substrates as photoanode in photoelectrochemical (PEC) solar cell.

Thin films of CdSe were deposited on to glass and titanium substrates using the method of spray pyrolysis. Aqueous solutions of cadmium chloride (CdCl_2) and selenourea ($\text{NH}_2\text{CSeNH}_2$) were mixed thoroughly and sprayed onto the heated substrates. Two types of films were deposited; in 1C1S-series, 1 part of CdCl_2 and 1 part of $\text{NH}_2\text{CSeNH}_2$ and in 1C2S series, 1 part of CdCl_2 and 2 parts of $\text{NH}_2\text{CSeNH}_2$ were taken. The deposition parameters such as substrate temperature, spray rate, concentration of starting solutions etc. were optimised for obtaining films of good crystallinity and PEC performance.

CdSe_{1-x}Te_x films have been deposited by using electron beam evaporation and electrodeposition. Single phase CdSe_{1-x}Te_x films in the entire composition range were prepared by evaporating the source material in the form of pellet with the help of electron beam. The pellet was prepared by taking appropriate amount of CdSe and CdTe power, mixing them thoroughly and pressing.

Sprayed CdSe Films

The films were deposited at substrate temperature ranging from 200 to 400°C. X-ray diffraction studies showed that the films deposited at 220°C and 350°C had the best crystallinity for films on titanium and glass substrates respectively. The reflections from (110) and (002) planes were most prominent for 1C1S and 1C2S films respectively. The 1C1S films showed predominantly hexagonal while 1C2S films showed both hexagonal and cubic phases.

The absorption edge in the transmission spectra was found to be sharper for 1C1S than 1C2S films, which indicated better crystallinity for 1C1S films. The band gap was obtained by plotting $(\alpha h\nu)^2$ vs $h\nu$, which was a straight line implying direct allowed transition. The absorption coefficient was in the range of 10^4 to 10^5 cm⁻¹ near the absorption edge. The PL spectra of as-deposited films showed single luminescence peak around 1.02 μ m corresponding to the impurity absorption.

X-ray diffraction techniques has been used to study crystallinity and orientation of the films. The compositional analysis of the films were done with XPS (X-ray photoelectron spectroscopy) and Auger spectroscopy. The optical reflection and transmission measurements were made to study the band gap of the films. The photoluminescence measurements were done at 10°K to obtain information about impurity levels. The refractive index was calculated by solving reflection and transmission equations in the Tomlin's form with the help of a computer using Newton-Raphson method. The resistivity of the as-grown films were low which increased by several order after annealing the films in air. XPS studies of the films showed to the binding energies of cadmium and selenium in agreement with the reported values for CdSe.

CdSe_{1-x}Te_x Films

Thin films of CdSe_{1-x}Te_x were deposited in the entire composition range. X-ray diffraction studies showed cubic zinc blende face throughout the composition range with preferred orientation in (111) direction. Except CdTe in which Te (101) phase was detected, all other films were single phase in nature. The lattice parameters varied linearly with composition and followed Vegard law. On annealing the CdSe rich CdSe_{1-x}Te_x films, a phase transformation from cubic to hexagonal was observed.

The optical reflection and transmission studies have been done throughout the composition range. The transmission spectra showed absorption edge corresponding to the band gap of respective composition. A decrease in sharpness in the absorption edge was observed for high x in $\text{CdSe}_{1-x}\text{Te}_x$ films which was attributed to the presence of free Te in these films. The $\text{CdSe}_{0.8}\text{Te}_{0.2}$ films deposited at substrate temperature lower than 200°C showed extension of transmission to lower wavelengths. All the films showed direct nature of transition, and yielded a straight line by plotting $(\alpha h\nu)^2$ vs. $h\nu$ from which the band gap was obtained. The band gap was found to vary nonlinearly with the composition which showed a minimum around $x = 0.6$. The UV-reflectance and its derivative with respect to wavelength were measured in the entire composition range which showed transitions other than band gap.

The refractive index showed peak corresponding to the fundamental absorption edge of the respective composition. The refractive index was found to increase with the substrate temperature for $\text{CdSe}_{0.8}\text{Te}_{0.2}$ films.

The photoluminescence (PL) measurements of the as deposited film showed only one luminescence peak throughout the composition range. The peak position did not vary much with the composition. The half width remained constant upto $x = 0.6$ and increased beyond it. The effect of air-

annealing on PL-spectra has been studied. Peak corresponding to the edge emission was observed for air-annealed films.

All the electron beam evaporated films were found to be n-type. The resistivity of the films was found to increase with the composition and substrate temperature.

Sprayed CdSe and electron beam evaporated CdSe_{1-x}Te_x films deposited on titanium substrates were used as photoanodes in photoelectrochemical cell. The electrolyte concentration was optimised against the cell performance and stability. The electrolyte containing 2.5M Na₂S, 1M S and 1M NaOH was found to be optimum. As-deposited films showed little photoelectrochemical behaviour. Air-annealing followed by etching improved the performance drastically. Annealing temperature was optimised against the open-circuit voltage and short circuit current. Annealing temperature 450°C and 400°C were found to be optimum for sprayed and electron beam evaporated films respectively.

Efficiencies in the range of 3-5% and 1.5-2.5% were obtained using sprayed 1C1S and 1C2S photoanodes respectively. The best cell parameters obtained using 1C1S photoanode in 2.5M Na₂S, 1M S and 1M NaOH electrolyte were: $V_{oc} = 575$ mV; $J_{sc} = 15.8$ mA/cm²; F.F. = 0.38 and $\eta = 4.93\%$. Conversion efficiency less than 2% was obtained using

electron beam evaporated photoanodes. A typical CdSe_{0.8}Te_{0.2} photoanode showed $V_{oc} = 550$ mV; $J_{sc} = 6.0$ mA/cm²; F.F = 0.28 and $\eta = 1.85\%$. The poor performance shown by these electrodes was attributed to the high resistivity and low grain size in the films. A further decrease in the performance was observed for films with high x values.

The effect of light intensity on the cell performance was studied. For unetched electrodes the current density saturated at lower intensity indicating higher recombination losses at the surface which extends to higher illumination after etching. The V_{oc} varied linearly with logarithm of intensity from which junction ideality factor $n = 1.73$ was calculated for 1C1S photoanodes. The fill factor decreased with intensity.

The spectral response measurements were performed by measuring short-circuit current at different wavelengths at constant intensity. After etching the electrode, the spectral response showed higher current gain in the longer wavelengths region. The spectral response using CdSe_{0.8}Te_{0.2} photoanode covered wider portion of the solar spectrum than CdSe photoanode. The band gap obtained by plotting I^2 vs $h\nu$ were 1.66 eV and 1.5 eV for CdSe and CdSe_{0.8}Te_{0.2} photoanodes respectively which were in agreement with that obtained by optical studies.

The flat band potential measurements were done using sprayed and electron beam evaporated photoanodes by plotting J^2 vs. $V(\text{Vs.SCE})$ under monochromatic light illumination. The values of V_{fb} obtained for different electrodes were: -1.54V (Vs.SCE), -1.55 (Vs.SCE) for 1C1S and 1C2S sprayed CdSe respectively and -1.3 V(Vs.SCE) for evaporated $\text{CdSe}_{0.8}\text{Te}_{0.2}$ photoanode. The Mott-Schottky curve was obtained by plotting $1/C^2$ Vs $V(\text{Vs. SCE})$ for 1C1S sprayed CdSe. The various parameters calculated using the curve were the flat band potential $V_{fb} = -1.5$ V(Vs.SCE); the carrier concentration $N_D = 2.26 \times 10^{16} \text{cm}^{-3}$; the redox potential of electrolyte $V_{f,redox} = -0.75$ V(Vs.SCE); the band bending $V_b = 0.75$ V; the depletion layer width $W = 0.192$ μm ; conduction band edge $E_c = -1.6$ V(Vs.SCE); the valance band edge $E_v = +0.08\text{V}$ (Vs.SCE). Using these values a band diagram has been drawn for CdSe sulphide-polysulphide electrolyte system.

Stability and photodegradation studies were done using sprayed and evaporated films. After exposing the electrode in the electrolyte, the Auger spectrum showed sulphur peak at 150 eV indicating sulphur substitution at the surface. X-ray diffraction of electrode before and after dipping in the electrolyte showed that the peak heights decreased after dipping which was attributed to the formation of amorphous Cd-S on the electrode surface. A deterioration in stability was observed at higher illumination intensity and low polysulphide concentration.

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