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PHOTOELECTROCHEMICAL CHARACTERISTICS OF BRUSH ELECTRODEPOSITED $CdSe_xTe_{1-x}$ THIN FILMS

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CdSexTe1-x thin films were brush plated on titanium and conducting glass substrates from the precursors at different substrate temperatures in the range of 30 - 80°C. X-ray diffraction studies indicated the films to possess hexagonal structure irrespective of composition. The strain and dislocation density decrease with increase of substrate temperature. The crystallite size increased from 30 – 100 nm as the substrate temperature increased. Optical band gap of the films varied in the range of 1.45 – 1.72 eV. Photoelectrochemical cells were made with the electrodes of different composition. The photo output was nearly equal to earlier reports.

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1. Introduction

CdSe and CdTe form a solid solution throughout the entire composition in the compound CdSexTe1-x. This ternary is a very important candidate for photoelectrochemical cells. They can also be used for the photo-assisted decomposition of water [1]. Hodes et al. [2,3] have obtained solar conversion efficiencies up to 8% by using a liquid junction cell based on $CdSe_{0.65}Te_{0.35}$ polycrystalline thin film as the active electrode. In $CdSe_xTe_{1-x}$ ternary compounds the crystal structure and the band gap can be modified by changing the value of x. Normally CdSe and CdTe exhibit hexagonal wurtzite structure and cubic zinc blende structures, respectively. $CdSe_xTe_{1-x}$ films have been prepared by different techniques such as thermal evaporation [4], slurry painting [3], two source evaporation of CdSe and CdTe [5], electron beam evaporation [6], hot wall deposition technique [7,8], electrodeposition [9], brush plating [10], pulse plating [11] etc. In this work, the brush plating technique was employed for the deposition of thin films on conducting glass and titanium substrates at different temperatures in the range 30 - 80°C and the electrical, structural and optical properties are presented and discussed. In an earlier report on brush plated $CdSe_xTe_{1-x}$ films, the films were deposited, at room temperature and the photoelectrochemical properties were presented [10].

2. Experimental

Thin films of $CdSe_xTe_{1-x}(0<x<1)$ were deposited on titanium and conducting glass substrates baths maintained at different temperatures in the range 30 - 80°C. The deposition bath consisted of 0.1M $CdSO_4$, 0.001M TeO_2 and 0.001M SeO_2. Tin oxide coated conducting glass substrates(5 ohms/sq) and Titanium substrates were used. The deposition current density was 100 mA cm^{-2} and graphite was the anode. The temperature of the substrate was varied in the range

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of 30 - 80°C. The thickness and surface roughness of the films was estimated by Mitutoyo surface profilometer. Structural analysis of the films was made by JEOL 8030 model x-ray diffractometer using CuKα radiation. Optical band gap was estimated from the absorption spectra using an Hitachi U3400 UV-Vis-NIR spectrophotometer. Surface morphology of the films were observed by the Molecular Imaging systems Atomic force microscope. EDAX measurements were made using a JOEL SEM with an EDAX attachment. Photoelectrochemical measurements were made using a 250W tungsten halogen lamp. Hot probe measurements were made by placing the film over an aluminium plate and an aluminium probe was connected to the aluminium plate through a multimeter. The aluminium probe was heated by a 25W soldering iron, and while this probe was hot, it was momentarily contacted with the film. The multimeter showed a reading, and depending upon the sign of the reading, the type of the semiconductor was identified.

The brush plating technique also known as selective plating, differs from traditional tank or bath plating in that the work piece is not immersed in a plating solution (electrolyte) instead, the electrolyte is brought into contact with the part and applied by a hand-held anode or stylus, which incorporates an absorbent wrapping for applying the solution in the work piece (cathode). A direct current power pack drives the electrochemical reaction, depositing the desired metal on the surface of the substrate. In practice, movement between the anode and cathode is required for optimum results when plating,stripping, activating and so on. Currently, a broad range of metals can be plated by brush plating. The key advantage of brush plating is portability. Many systems can be moved to various locations in a production facility or be transported to the job site. Selective plating is also versatile: it permits most electroplate types to be deposited onto any conductive substrate that can be touched with an electrode. Cast iron, copper, stainless steel and aluminium can be plated by this method and exhibit good adhesion. Limited adhesion can be obtained with other materials such as titanium, tungsten and tantalum.The schematic of the system is given elsewhere[11]. The cotton wrapped graphite anode was soaked in the precursor solution and brushed on the cathode at the rate of 2 cm/min. Uniform pressure was applied on the cathode surface while moving the anode, this resulted in uniform thickness. Thickness and surface roughness of the films estimated from surface profilometer were in the range of 1.5 – 2.0 μm and 1.5 – 3.4 nm respectively with increase of substrate temperature.

3. Results and discussion

The films deposited at different substrate temperature have exhibited all the peaks corresponding to the hexagonal phase. The peaks corresponding to (100),(002),(101),(102),(110),(103),(112), (203),(105) and (300) were observed in all the cases. The lattice parameters were evaluated using the expression

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

where h, k, l are the lattice planes and d is the interplanar spacing determined using Bragg's equation. The lattice constant increased with substrate temperature. The change of lattice constant with substrate temperature clearly indicated that the crystallites were under stress, leading to either elongation or compression of the lattice constant. This might be due to the change of density and nature of native imperfections with the deposition temperature of the film [12].

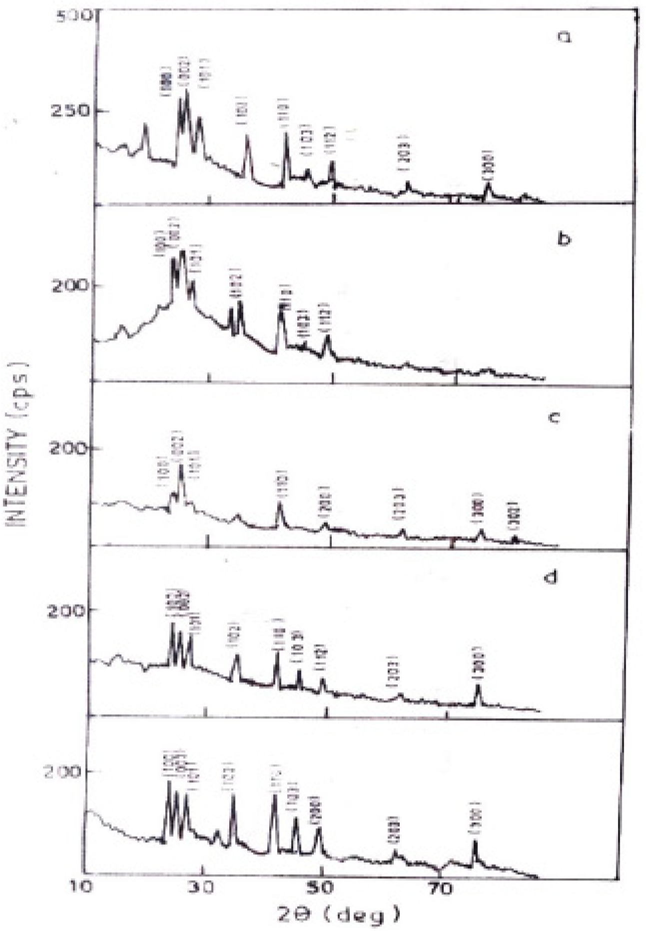


Fig. 1. X-ray diffraction pattern of CdSe$_x$Te$_{1-x}$films deposited at different substrate temperatures (a) 80°C (b) 60°C (c) 50°C (d) 40°C (e) 30°C.

The dislocation density (δ) was determined using the relation [13]

$$\delta = 15\beta \cos\theta/4aD \qquad (2)$$

where β is the full width at half maximum and D is the crystallite size. The variation of dislocation density with substrate temperature is also indicated in Table-I. It was observed that the dislocation density decreased with the increase of deposition temperature. This might be due to the improvement in crystallinity.

Optical absorption measurements were made on the films deposited on conducting glass substrates(Fig.2). The bandgap estimated from the Tauc's plot was in the range of 1.72 – 1.45 eV as the substrate temperature increased, the concentration of tellurium increased in the CdSexTe1-x films resulting in CdTe rich films(Table-II), hence the band gap of the films shifted towards CdTe. These values are in agreement with earlier reports[6,8,9]. Moreover, the grain size of the films increase with increase of substrate temperature. Hence for smaller grain size the band gap is higher due to quantum size effects.

Surface morphology of the films was studied by Atomic force microscopy. The surface of the films was uniform with the grain size increasing with increasing of deposition temperature(Fig.3). It increased from 30 nm – 100nm as the deposition temperature increased. The surface roughness increased from 1.83 – 3.25 nm with increase of deposition temperature.

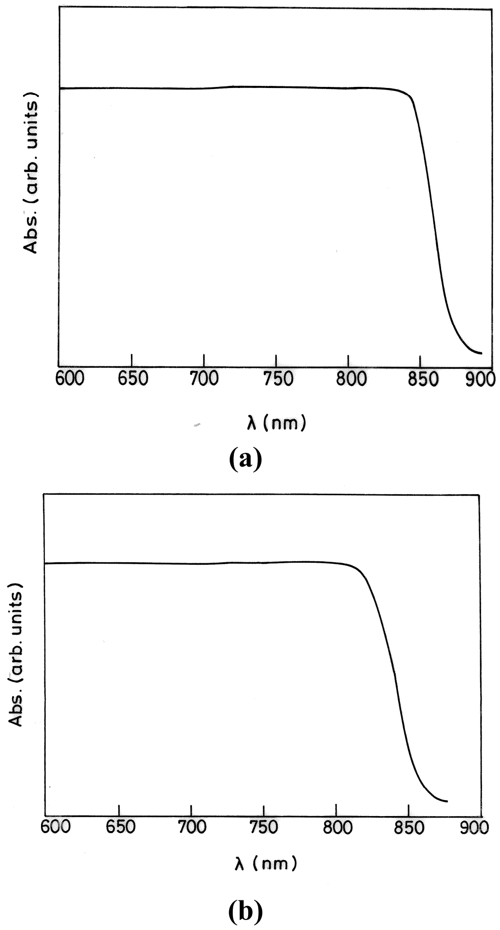


Fig. 2. Absorbance spectra of $CdSe_xTe_{1-x}$ films deposited at different substrate temperatures (a) 80°C (b) 40°C

Hot probe measurements indicated the films to be n-type. Hall measurements were made on the films adopting the procedure reported earlier [14]. In this method the CdSeTe layer is mechanically transferred from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [15]. The electrical properties of the CdSeTe layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method. Vacuum evaporated Indium served as the ohmic contact. The value of the resistivity determined from Van der Pauw method varied from 10^4 to 10^2 ohm cm as the substrate temperature increased (CdTe concentration in the CdSeTe films increased). Hall measurements also indicated the films to be n-type. The carrier density, mobility and resistivity of the films of different substrate temperature are shown in Table-II.

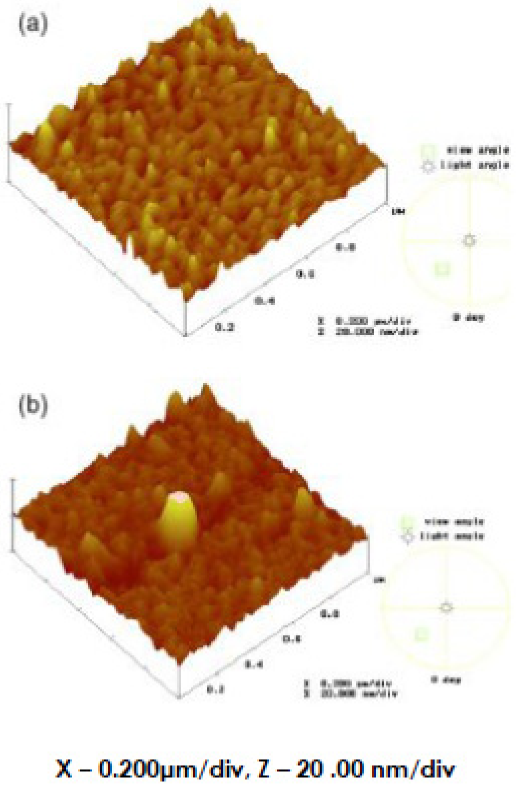
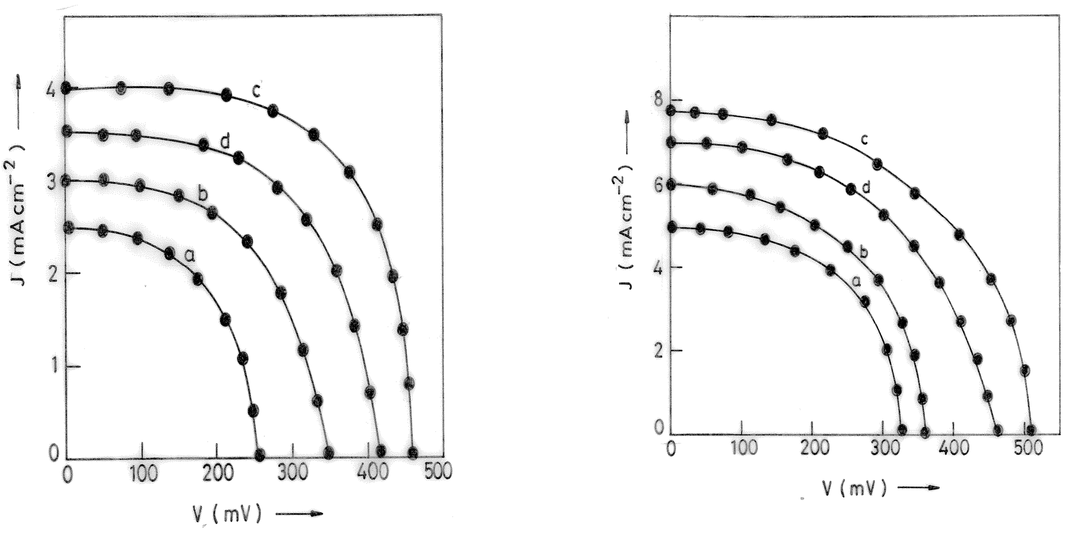


Fig. 3. Atomic force micrographs of $CdSe_xTe_{1-x}$ *films deposited at different substrate temperatures (a) 80°C (b) 50°C..*

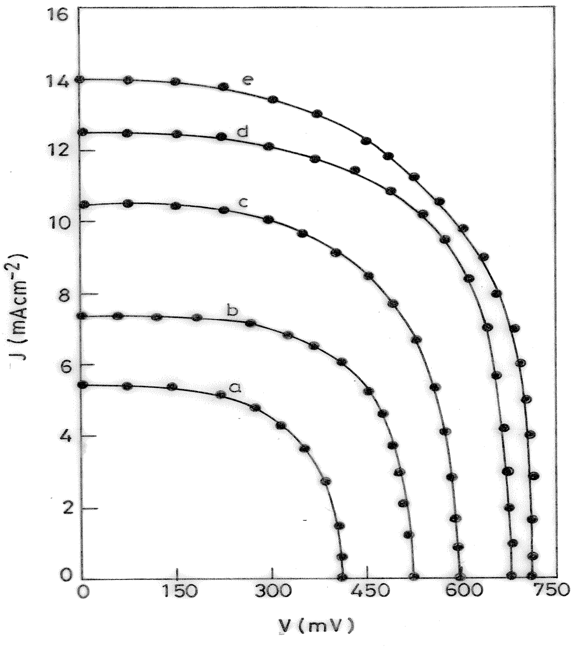
The power output characteristics were obtained for the PEC cells using the photo electrodes of different composition and heat treated at different temperatures. Fig.4 shows the load characteristics of the electrodes of different composition heat treated at different temperatures. It was observed that the PEC output was high for electrodes heated at 525°C irrespective of composition. Photoelectrodes heat treated beyond 525°C exhibited lower V_{oc} and J_{sc} values due to change in concentration of tellurium and selenium vacancies as well as reduction in thickness. Amongst the electrodes of different compositions, it was observed that the overall output started to increase as the selenium content increased in the material. Electrodes with the composition $CdSe_{0.6}Te_{0.4}$ exhibited the maximum PEC output; hence, further studies were made on the films of this composition.

The load characteristics for the films of this composition is shown in Fig.5. This value is lower than the reported value of 0.75 V for electrodes prepared by sintering mixture of CdTe and CdSe [16], but the J_{sc} value for this composition is higher. The value of J_{sc} is higher than that reported for the brush plated electrode [8]. At intensity values beyond 80 mW cm^{-2}, V_{oc} was found to saturate as is commonly observed for photovoltaic and PEC cells, J_{sc} was found to increase with increase in intensity of illumination. A plot of $\ln J_{sc}$ versus V_{oc} yielded a straight line. Extrapolation of the line to the y-axis yields a J_0 value of 10^{-7} A cm^{-2}, the ideality factor was calculated from the slope of the straight line and it was found to be 1.88. The effect of photoetching on the PEC performance



$CdSe_{0.1}Te_{0.9}$

$CdSe_{0.4}Te_{0.6}$



$CdSe_{0.9}Te_{0.1}$

Fig. 4. Load characteristics of $CdSe_xTe_{1-x}$ films post heat treated at different Temperatures (a) 450°C (b) 500°C (c) 525 °C (d) 550°C.

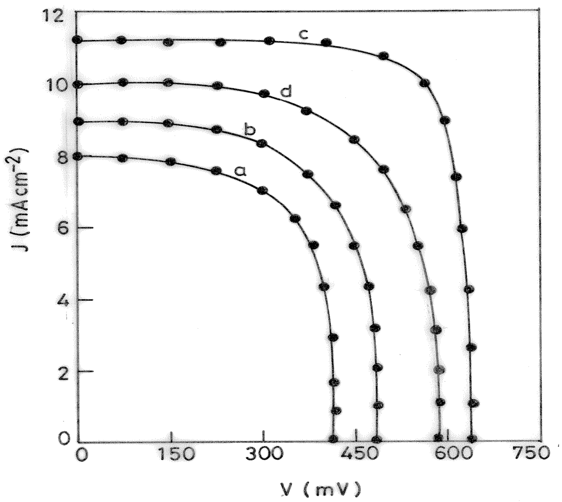


Fig.5. Load characteristics of CdSe$_{0.6}$Te$_{0.4}$ films heat treated at different temperatures (a) 450°C (b) 500°C (c) 525 °C (d) 550°C.

was studied by shorting the CdSe$_{0.6}$Te$_{0.4}$ photoelectrode and the graphite counter electrode under an illumination of 100 mW cm^{-2} in 1:100 HCl for different durations in the range 0 – 100 s. Both the photocurrent and photovoltage are found to increase upto 80 s photoetch, beyond which they begin to decrease (Fig.6). Photoetching leads to selective attack of surface defects not accessible to chemical etchants. It is observed that during photoetching the V_{oc} increased from 0.675 V to 0.72 V and J_{sc} increased from 12.5 mA cm^{-2} to 14.5 mA cm^{-2}. The decrease in photocurrent and photovoltage beyond 80s photoetching can be attributed to separation of grain boundaries due to prolonged photoetching [17]. The power output characteristics (Fig.7) after 80s photoetching indicates a V_{oc} of 0.72 V, J_{sc} of 14.5 mA cm^{-2}, ff of 0.72, η of 7.81% for 80 mW cm^{-2} illumination. The photovoltaic parameters of the electrodes of different composition are shown in Table III.

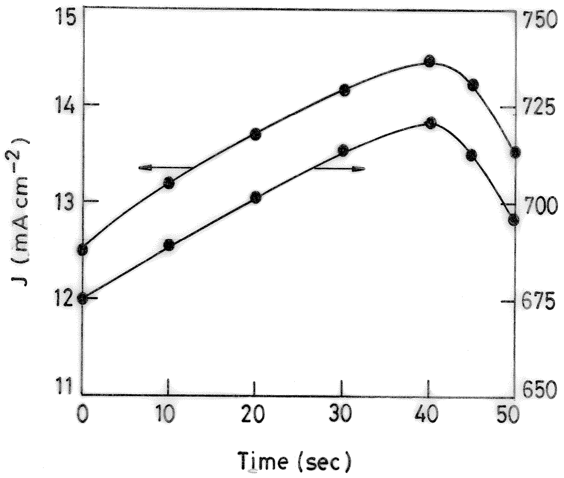


Fig. 6. Effect of photoetching on the open circuit voltage and short circuit current of CdSe$_{0.6}$Te$_{0.4}$ films heat treated at 525 °C

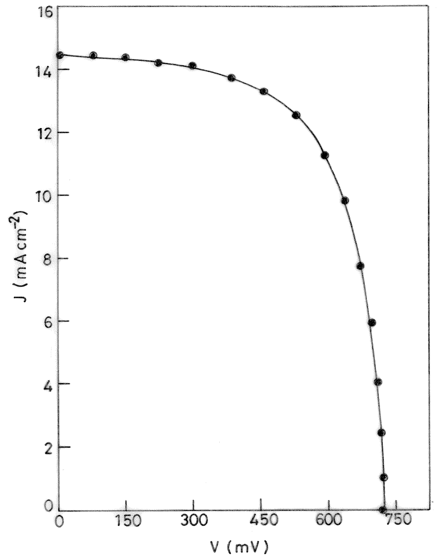


Fig. 7. Load characteristics of $CdSe_{0.6}Te_{0.4}$ *films heat treated at 525 °C after photoetching for 80s.*

4. Conclusions

The brush plating technique can be successfully employed for the deposition of $CdSe_xTe_{1-x}$ films, n-type films with resistvity in the range of $10^4 - 10^2$ ohm cm can be easily obtained. In this study hexagonal structure has been obtained for all the films. Films with crystallite size in the range of 30 – 100nm can be obtained. Photo outputs can be further increased by doping.

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