PHOTOELECTROCHEMICAL PROPERTIES OF CdS_xTe_{1-x} FILMS

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 CdS_xTe_{1-x} films were deposited on titanium and conducting glass substrates at room temperature using 0.25 M cadmium sulphate, the concentration of sodium thiosulphate and TeO2 dissolved in sodium hydroxide was varied in the range of 0.01–0.05 M. The as deposited films exhibited hexagonal structure irrespective of the composition. The FWHM maximum of the x-ray diffraction peaks were found to decrease with increase of duty cycle. The optical energy gap values are in the range of 1.54–2.32 eV for films of different composition, it is observed that the band gap shifts towards CdS side as the concentration of CdS in the films increase. Photoelectrochemical cell studies indicated higher short circuit current density and efficiency compared to earlier reports.

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1. Introduction

Photovoltaic solar energy conversion is a very attractive alternative to fulfill the increasing energy demands. Several efforts have been made to obtain high efficiency low cost solar cells based on CdS/CdTe heterostructure. The highest efficiency reported so far with this system is 16 %[1], but theoretically efficiency around 30 % has been theoretically predicted[2]. One of the factors that have been associated with the limited efficiency of CdS/ CdTe solar cells is the existence of a composition graded CdS / CdTe interface generated by an intermixing process during the process of production [3]. Therefore, a full understanding of the CdS_xTe_{1-x} mixed system is warranted. Earlier several techniques like PVD[4,5], chemical deposition[6], pulse laser deposition[7],slurry coating[8] etc have been employed for the deposition of CdS_xTe_{1-x} films. In this work, CdS_xTe_{1-x} films were deposited for the first time by the pulse plating technique. The details of pulse plating are given in our earlier paper[9]. In this paper we report the photoelectrochemical properties of CdS_xTe_{1-x} films.

2.Experimental methods

 CdS_xTe_{1-x} films were deposited on titanium and conducting glass substrates of size 2 cm long and 1 cm wide, at room temperature using 0.25 M cadmium sulphate, the concentration of sodium thiosulphate and TeO₂ dissolved

in sodium hydroxide was varied in the range of 0.01-0.05 M. As an example, for the deposition of $CdS_{0.5}Te_{0.5}$ film, the precursors with the following concentration, 20 ml of 0.25 M CdSO₄, 1 ml of 0.025 M TeO₂ and 1 ml of 0.025 M sodium thiosulphate were taken. All chemicals were of Analar grade purity. The pH of the bath was adjusted to 2.0 by adding sulphuric

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acid. The deposition potential was maintained at -0.80 V (SCE). The conducting glass and titanium substrates were cleaned prior to deposition. The duty cycle was varied in the range of 6–50%. The deposition time was 60 min in all the cases. Thickness of the films estimated by Mitutoyo surface profilometer was 2.0 μ m. Uniformity of the deposit was found by measuring the resistivity profile across the deposit and it was observed that the resistivity varied within 0.3%. The films were characterized by x-ray diffraction using a PANalytical x-ray diffractometer. Optical absorption measurements were made on the films deposited on conducting glass substrates

using Hitachi U3400 UV–VIS–NIR spectrophotometer. Photoelectrochemical cell studies were made on the films of different composition using 1M polysulphide as the redox electrolyte.

3. Results and discussion

The as deposited films exhibited hexagonal structure irrespective of the composition. Results on pulsed laser deposited CdSTe films indicated that the films deposited below x = 0.5 in CdS_xTe_{1-x} films exhibited cubic structure, whereas films deposited at values greater x = 0.5 exhibited hexagonal structure[5]. For screen printed CdS_xTe_{1-x} films, films exhibited cubic structure for higher values of x[8]. In this study only single phase hexagonal structure was observed for all compositions. The FWHM (Fullwidth at half maximum) of the XRD peaks were found to decrease with increase of duty cycle. Fig. 1 shows the XRD pattern of the CdS_{0.5}Te_{0.5} films deposited at different duty cycles. Peaks corresponding to CdS or CdTe were absent. The peaks were observed to shift towards low 2 θ side as the concentration of CdTe increased in the ternary. The intensity of the peaks increased with increase of duty cycle. This may be attributed to the fact that as the duty cycle increases, the thickness of the films increase, hence the intensity



Fig.1. X-ray diffraction pattern of the CdS0.5Te0.5 films deposited at different duty cycles: (a) 10%; (b) 15%; (c) 33%; (d) 50%.

of the peaks increase. The peaks corresponding to the (100), (00 2), (101), (102), (110) and (112) reflection were observed in all the cases. The peaks were found to shift from CdTe to CdS side as the concentration of CdS increased in the films. Fig. 2 shows the variation of lattice spacing of CdS with increase of CdTe concentration. The lattice parameters were evaluated using the equation



$$1/d^2 = 4/3a^2(h^2 + hk + k^2) + l^2/c^2$$

Fig.2. Variation of lattice spacing of CdS_xTe_{1-x} films with CdTe Concentration

The variation is linear and obeys Vegard's law. The lattice parameters changed from CdTe to CdS side as the concentration of CdS increased in the films. Large crystallites produce sharp peaks, while, very tiny crystallites produce broad XRD peaks. Small crystallites allow x-ray beam to diverge as it leaves since the diffraction peaks are no longer infinite in length as compared to the incident wavelength. Thus, these crystallites do not collimate the x-ray beam as effectively as large crystallites and hence produce a broad diffraction peak. Optical absorption studies were made on the films of different composition deposited at a duty cycle of 50% on conducting glass substrates. Plots of $(ahv)^2$ vs hv are shown in Figs. 3 and 4. The plots were linear suggesting direct band nature of the films of different composition, it is observed that the band gap shifts towards CdS side as the concentration of CdS in the films increase vary from 1.44 to 2.41 eV as the percentage of CdS increased. Similar results were observed for chemically deposited films, screen printed films and pulse laser deposited films[6 – 8].



Fig. 3. $(ahv)^2$ vs hv plot for CdS_xTe_{1-x} films of different composition deposited at 50 % duty $cycle(a) \ x = 0.1$ (b) x = 0.2 (c) x = 0.3 (d) x = 0.4 (e) x = 0.5 (f) x = 0.6.



Fig.4. $(ahv)^2$ vs hv plot for CdS_xTe_{1-x} films of different composition deposited at 50 % duty cycle(a) x = 0.7 (b) x = 0.8 (c) x = 0.9.

The power output characteristics were obtained for the PEC cells made using the photo electrodes of different compositions and heat-treated at different temperatures Fig.5 shows the load characteristics of the post heat treated electrodes of different composition. Photoelectrodes heat treated beyond 525°C exhibited lower V_{oc} and J_{sc} values due to change in concentration of sulphur and tellurium 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 sulphur content increased in the material. Electrodes with the composition $CdS_{0.9}Te_{0.1}$ exhibited the maximum V_{oc} of 0.55 V and 13.2 mA cm⁻² for 80 mWcm⁻² illumination. These values are higher than the reported value for electrodes prepared by chemical bath deposition[9].

The variation of V_{oc} and J_{sc} with intensity indicated that the V_{oc} increased from 0.35 – 0.57 V as the intensity of illumination increased from 20 – 100 mW cm⁻² J_{sc} was found to increase with increase in intensity of illumination. It was observed that J_{sc} increases from 2.90 mAcm⁻² to 17.0 mAcm⁻² as the intensity of illumination increased from 20 to 100 mW cm⁻². Since the electrode of composition CdS_{0.9}Te_{0.1} showed maximum voltage output, further studies were

made on the electrodes of this composition. A plot of $\ln J_{sc}$ versus V_{oc} (Fig.6) yielded a straight line. The value of the ideality factor was calculated from the slope of the straight line and it was found to be 1.80. The reverse saturation

current density, J_o , was 2 x 10^{-7} Acm⁻². The effect of photoetching on the PEC performance was studied by shorting the photoelectrode and the graphite counter electrode under an illumination of 80 mWcm⁻² in 1:100 HCl for different



Fig.5. Load characteristics of CdS_xTe_{1-x} films deposited at 50 % duty cycle

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.7). Photoetching leads to selective attack of surface defects not accessible



Fig. 6. lnJ_{sc} versus V_{oc} plot of $CdS_{0.9}Te_{0.1}$ films deposited at 50 % duty cycle and post heat treated at 525 °C

to chemical etchants. It is observed that during photoetching the V_{oc} increased from 0.55 V to 0.62 V and J_{sc} increased from 13.2 mAcm⁻² to 16.00 mAcm⁻². The decrease in photocurrent and photovoltage beyond 80 s photoetching can be attributed to increase in surface area due to prolonged photoetching [77]. The power output characteristics (Fig.8) after 80 s photoetching indicates a V_{oc} of 0.62 V, J_{sc} of 16.00 mA cm⁻², ff of 0.76, η of 9.55% for 80 mWcm⁻² illumination. The photovoltaic parameters of the electrodes of different composition are shown in Table 1. The short circuit current density and efficiency of the photoelectrodes are higher than the earlier reports for the electrodes of composition CdS_{0.9}Te_{0.1}[9]. The highest value of cell output obtained with the electrodes of



Fig.7. Variation of V_{oc} and J_{sc} of $CdS_{0.9}Te_{0.1}$ films deposited at 50 % duty cycle and post heat treated at 525 °C after photoetching for different durations.



Fig.8. Load characteristics of $CdS_{0.9}Te_{0.1}$ films deposited at 50 % duty cycle and post heat treated at 525 °C after photoetching for 80s.

composition $CdS_{0.9}Te_{0.1}$ could be attributed to the larger value of the flat band potential. For a cell with n-type semiconductor photoelectrode, the larger the value of the flat band potential, the more negative is the value of V_{fb} and therefore greater is the possible output voltage and hence the maximum power conversion efficiency. The enhancement in the flat band potential may be caused due to the creation of the new donor levels by the substitution of S²⁻ ions by Te²⁻ ions which effectively shift the Fermi level increasing the amount of band bending and hence the open circuit voltage[10-12].

Conclusion

The results of this investigation clearly points to the possibility of preparing high efficiency CdS_xTe_{1-x} photoelectrodes.

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