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ELECTROCHEMICAL PHOTOVOLTAIC ACTIVITY OF ELECTRODEPOSITED CdS_xSe_{1-x} THIN FILMS

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INTRODUCTION

Photoelectrochemical solar cells (PESCs) are technically simple, are of low cost, have in-situ solar energy storage facility and have attracted considerable attention for many years [1, 2]. The ternary chalcogenide semiconductor CdS_xSe_{1-x} (0 < x < 1) is a potential candidate for PESCs whose bandgap(E_g) can be varied from 2.4 eV (CdS) to 1.7 eV (CdSe). Normal chemical and electrochemical routes for preparation of CdS [3 to 5] and CdSe [6 to 8] thin films have already been reported earlier but works on CdS_xSe_{1-x} are a few only [9 to 12]. The chemical-electrochemical technique appears to be more suitable for preparing tailor-made bandgap CdS_xSe_{1-x} films for large-area devices. Here, we report the details of electrodeposition of CdS_xSe_{1-x} films, its PESC performance and some of its properties.

EXPERIMENTAL DETAILS

CdS_xSe_{1-x} films were deposited galvanostatically on pre-cleaned Ti and conducting glass substrates which served as cathodes in a single-compartment, two-electrode electrochemical cell with Pt as counter electrode. The deposition solution consisted of 0.12 M each of

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CdSO₄, NH₂CSNH₂ and varying concentrations of Se as Na₂SeSO₃ [6] in mM range. The temperature of the solution was maintained at 55°C and was stirred continuously at a constant rate during deposition. Deposition was carried out for 35 minutes. Then, the films were washed, dried and post annealed in air at 350°C for varying time-periods. PESC studies using polysulphide electrolyte, under 50 mW/cm² intensity of illumination were carried out to optimise the deposition parameters.

Bandgaps for two different Se concentrations have been determined from optical absorption studies in the wavelength range 410 nm to 810 nm.

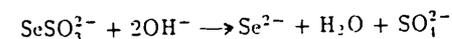
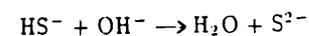
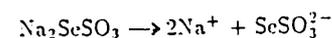
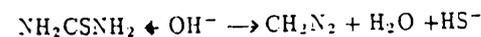
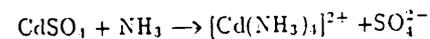
Electrochemical characterization was carried out by obtaining voltammograms in dark and under illumination from -950 mV_{SCF} to +500 mV_{SCF}.

RESULTS AND DISCUSSIONS

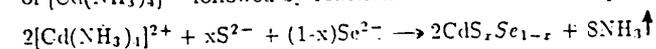
Figure 1(a and b) shows open-circuit photovoltage (V_{oc}) and short-circuit photocurrent density (J_{sc}) as functions of (i) Se concentration, (ii) electrolysis current density, (iii) pH and (iv) annealing time of CdS_xSe_{1-x} films used in PESCs with S₂²⁻, S²⁻ electrolyte. The optimum deposition parameters for reasonably good films were found to be : (i) Se concentration = 2.50 mM, (ii) electrolysis current density = 2.5 mA/cm², (iii) pH = 10 and (iv) annealing time = 2 min.

The film formation mechanism is assumed to proceed in the following steps [3, 4].

Formation of ions



The overall reaction at the cathode, acting as a catalyst, goes by the adsorption/deposition of [Cd(NH₃)₄]²⁺ followed by reaction with S²⁻ and Se²⁻ species.



In the bulk also a similar reaction follows leading to the formation of CdS_xSe_{1-x} par

which either settle down at the bottom of the beaker or are adsorbed at the electrodes. Adsorption of these particles at the cathode gives rise to an irregular surface morphology.

Higher Se concentration (either presence of greater amount of SeSO_3^{2-} species or higher electrolysis current) makes the film porous [12] resulting in poor photoresponse. Films with low Se concentration or low electrolysis current gave lower values of J_{sc} but higher values V_{oc} due to its higher bandgap (since $U_{ph,max} = E_g/e$ [1]). At lower pH, hydrolysis of NH_2CSNH_2 is slow [4] and lesser amount of S is present leading to Se rich films resulting in poor photoresponse. At higher pH (~ 13), S liberation is fast leading to S rich films [12]. Annealing in air increases grain size [10] and incorporates oxygen in the film. Oxygen incorporation increases photosensitivity. Both the effects increase photoresponse. However, annealing at higher temperature or higher annealing time results in a surface TiO_2 formation, thereby lowering photocurrent.

As $\text{CdS}_x\text{Se}_{1-x}$ is a direct bandgap semiconductor, the bandgaps have been estimated from extrapolation to zero absorption in the $(\alpha h\nu)^2$ Vs $h\nu$ plots shown in figure 2. The bandgaps have been found to be 2.24 eV and 1.76 eV for Se concentrations of 2.50 mM and 4.38 mM respectively, which is in good agreement with other reported results [12].

Electrochemical characterization was done by obtaining voltammograms in dark and under illumination shown in figure 3(a). An increase in dark anodic current without any sign of saturation in the region -550 mV_{SCE} to $+500$ mV_{SCE} is seen. The illuminated curve is similar but the current is higher. This indicates that this material is n-type [3] with high density of surface/deep traps as is inferred from the high unsaturated photoanodic current.

PESC parameters with the optimised $\text{CdS}_x\text{Se}_{1-x}$ film (shown in fig. 3(b)) are: $V_{oc} = 218$ mV, $J_{sc} = 1.62$ mA/cm², Fill-factor = 40 % and photoconversion efficiency = 0.25 %. Low photoconversion efficiency is mainly due to non-uniform surface morphology and high series resistance. Efforts are on to increase the efficiency by etching.

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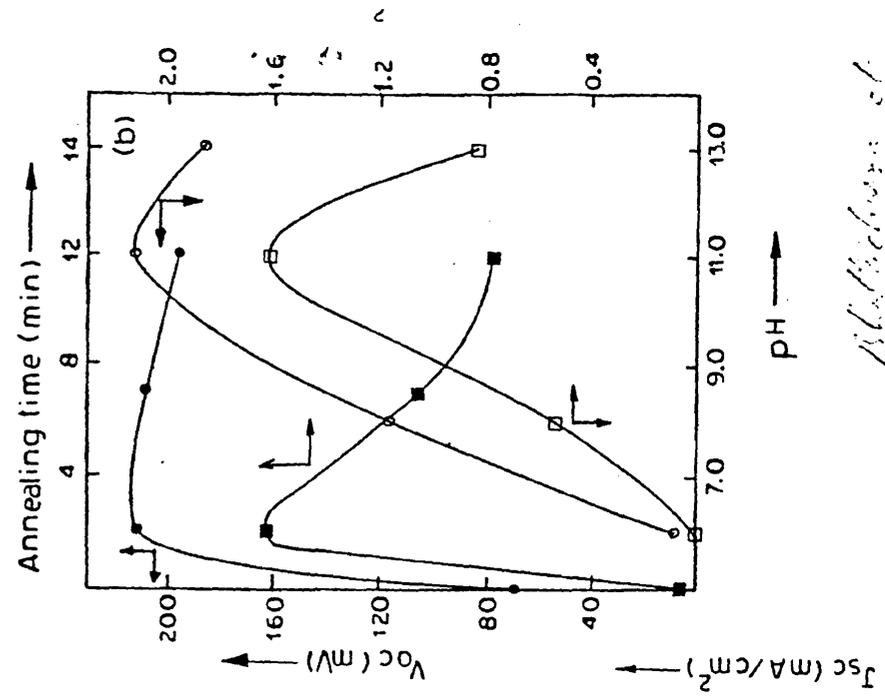
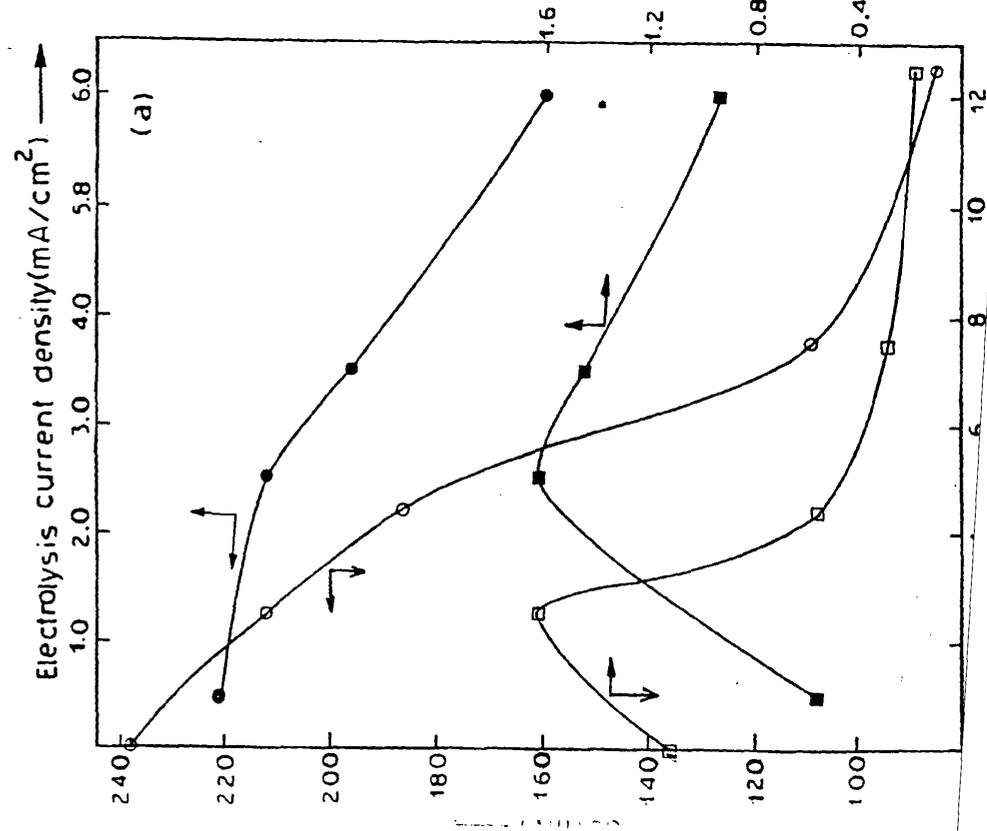
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Fig. 1 : Variation of V_{oc} and J_{sc} with (a) Se concentration and electrolysis current density and (b) pH and annealing time.

Fig. 2 : $(\alpha h\nu)^2$ Vs. $h\nu$ for two CdS_xSe_{1-x} films with Se concentrations of (1) 2.50 mM and (2) 4.38 mM.

Fig. 3 : (a) Voltammograms in dark (1) and under illumination (2) for CdS_xSe_{1-x} film in the region -950 mV_{SCE} to +500 mV_{SCE}.
(b) V_{ph} - J_{ph} characteristics of optimised CdS_xSe_{1-x} film.



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Fig. 3

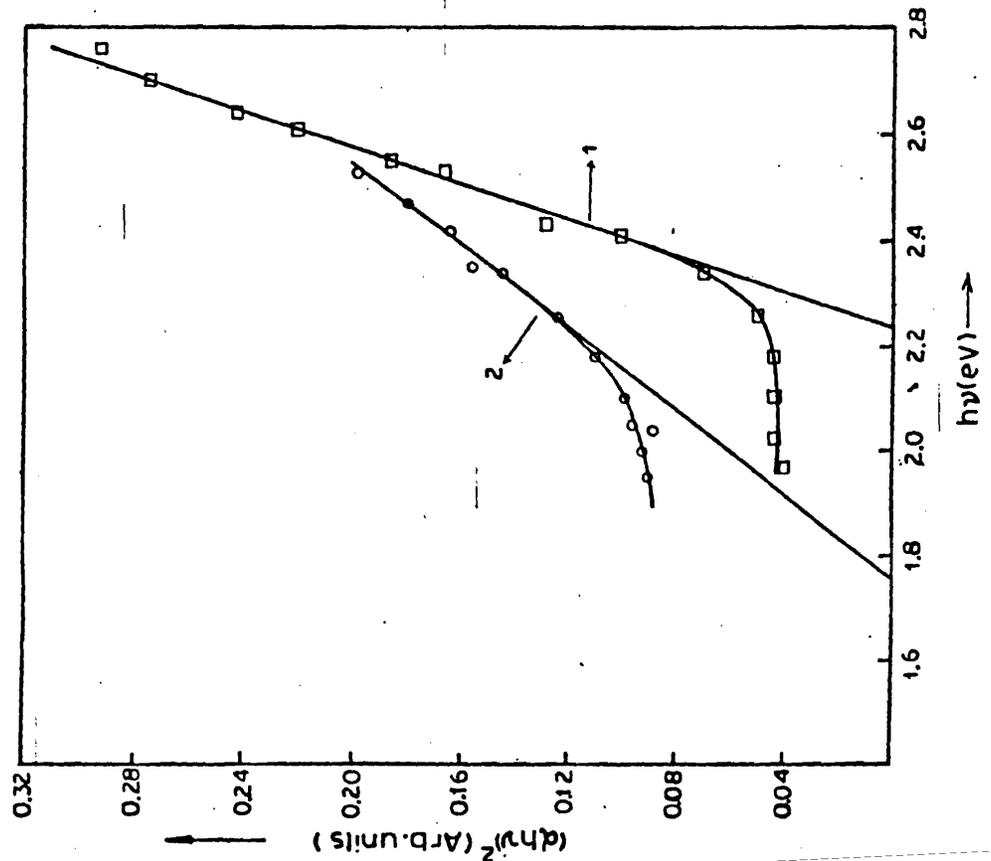
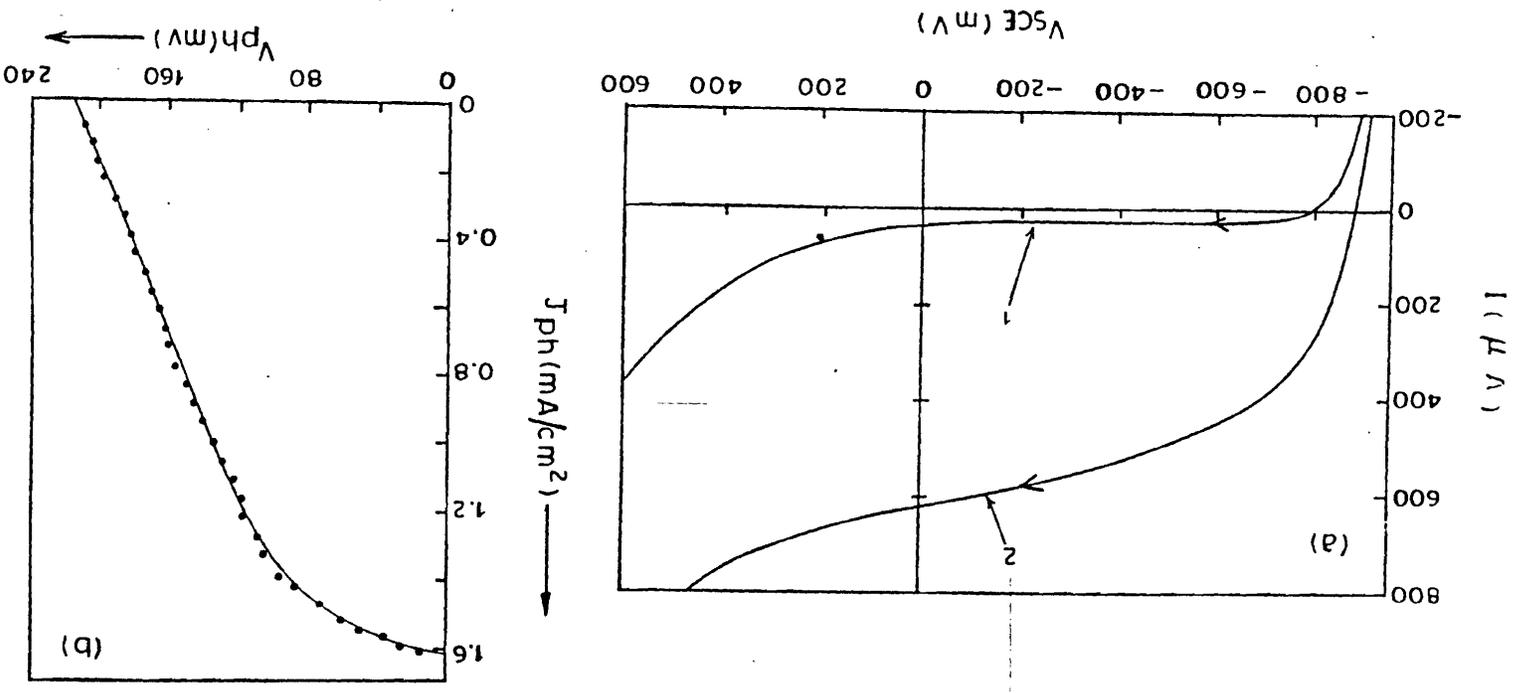


Fig. 2

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