

IMPROVED PERFORMANCE OF PHOTOETCHED CADMIUM SULPHIDE ELECTRODES IN PEC CELLS

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The photoelectrochemical cell comprising a chemically etched CdS single crystal electrode in 2M NaOH - 0.3M Na₂S-0.1M S gave $V_{oc} = 410$ mV, $J_{sc} = 0.64$ mA cm⁻² and $ff = 0.28$ under approximately 120 mW cm⁻² tungsten-halogen illumination. A short photoetching of the CdS electrode in a dilute HCl-HNO₃ mixture remarkably improved the photo output characteristics as follows: $V_{oc} = 520$ mV (18% increase), $J_{sc} = 2.33$ mA cm⁻² (68% increase) and $ff = 0.47$ (36% increase). The enhancement is a direct result of a reduction in the density of surface defects.

Key Words : Cadmium sulphide electrode, photoelectrochemical cell, photoetching.

INTRODUCTION

Recombination of electron and holes at a p-n junction, a Schottky-barrier or a heterojunction is known to adversely affect the device performance. At these junctions, recombination occurs mainly through interface states. Similarly in a photoelectrochemical (PEC) cell, presence of a wide variety of defects at a semiconductor surface inhibits the free flow of photogenerated minority carriers across the interface into the electrolyte. At these defects, the majority carriers get trapped and recombine with the minority carriers resulting in a decrease in the quantum efficiency of the photoelectrochemical cell.

Surface preparation, therefore, is crucial in all semiconductor devices. The surface damage from mechanical polishing is generally removed by chemical etching whereas complete removal of surface defects is not accomplished by this method. Chemisorption of transition metal ions [1] and surface oxidation [2] are known to reduce surface recombination by passivating sites responsible for electron-hole recombination. The technique of 'selective photoelectrochemical etching or photoetching' is of recent origin and has been successfully applied to improve the performance and output stability of various PEC cells [3-5]. In this communication, we report briefly on the current-voltage behaviour of chemically etched and photoetched CdS single crystal electrodes in alkaline sulphide-polysulphide electrolyte.

EXPERIMENTAL

Small single crystals of CdS (band gap 2.42 eV, $p = 1.36 \times 10^3$ ohm cm), cut from an ingot (grown by the Piper and Pollich method). The carrier concentration, calculated from the resistivity value, assuming an electron mobility of 200 cm² volt⁻¹ sec⁻¹ [6] was 2.29×10^{13} cm⁻³. The crystals were mechanically polished using alumina powder. An ohmic contact was provided by evaporating indium on the unpolished side and annealing for 30 mt. A copper wire was soldered to the indium surface and a thick layer of polystyrene coating was applied along the outer edge of the CdS electrode to restrict the electrolyte contact to the CdS surface alone.

The PEC cell consisted of the CdS working electrode and a platinum counter electrode in an argon purged 2M NaOH-0.3M, Na₂S-0.1M S redox electrolyte. Illumination was provided by a 250 W tungsten-halogen lamp (Oriol 6432). A 4 cm path length

circulating water filter and an IR absorbing filter (Oriol 7165) were placed in the path of the light to absorb the heat radiation. The light beam was focussed on the CdS surface by a condensing lens. The intensity of illumination at the photoelectrode measured by a Suryamapi (CEL) was approximately 120 mW cm⁻² which is uncorrected for absorption losses by the glass window and the redox couple. Optical absorption in CdS and the sulphide-polysulphide redox electrolyte was measured with a Hitachi U-3400 spectrophotometer.

Etching of the CdS surface

The chemical etching of the polished CdS surface was done in conc. HCl for 30 sec. The photoetching process consisted in shorting the chemically etched electrode to the counter electrode in the etchant solution made of diluted (10 times) mixture of HCl and HNO₃ in the volume ratio of 97:3, and illuminating the electrode at 120 mW cm⁻² for 30 sec.

RESULTS AND DISCUSSION

The optical absorption for the CdS crystal (0.06 cm thick) is shown in Fig.1 (curve-a). For comparison, the absorption by the redox is also shown in the same figure (curve-b). It is clear that the redox absorption overlaps that of CdS causing a substantial attenuation of the light intensity in the wavelength range of CdS absorption. To minimise such losses earlier workers [4] have used only Na₂S in the electrolyte. In the present experiments, however, both the sulphide and polysulphide species are used in the electrolyte to have a stable redox system.

The output power characteristics of the PEC cell using chemically etched and photoetched electrodes are shown in curves a and b of Fig.2. Also shown in the figure is curve c obtained after continuously illuminating the photoetched electrode for 1 hour under short-circuit conditions. For easy comparison, the values of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), obtained by dividing the current values by the electrode area, 0.06 cm², and fill factor (ff) are listed in Table I.

An examination of Fig.2 reveals that the PEC cell using the chemically etched electrode suffers from low values of J_{sc} and ff , the values (Table I) being 0.64 mA cm⁻² and 0.28 respectively. These results further suggest that there exists a large density of

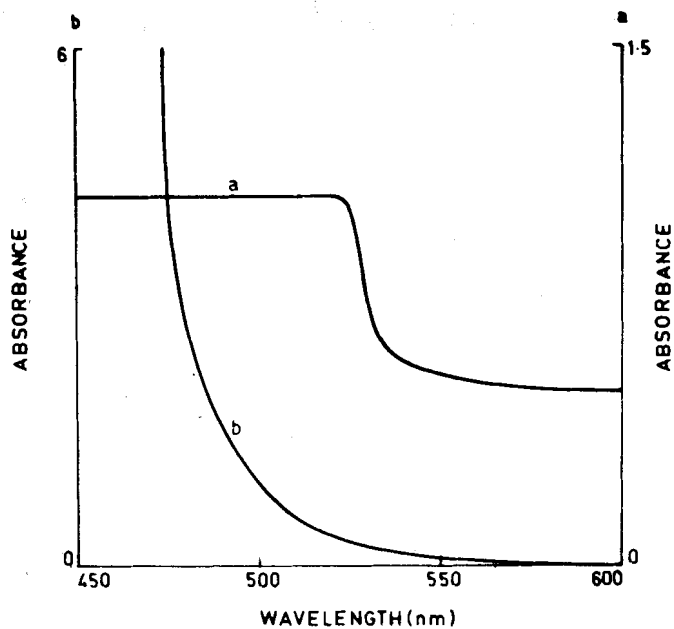


Fig. 1: Optical absorbance characteristics of the CdS crystal (curve a) and the redox electrolyte 2M NaOH-0.3M Na₂S-0.1M S (curve b).

surface states which act as sites for trapping electrons which eventually recombine with holes. Thus a large fraction of the electron-hole pairs created are lost in recombination. The marked effect of photoetching on the I-V output (Fig.2) showed an increase in V_{oc} by 18%, I_{sc} by 68% and ff by about 36%. These results are in accordance with similar findings [4] on CdS PEC solar cells. Curve c obtained after 1 hour illumination shows a further increase in V_{oc} and I_{sc} by 2.8 and 12.8% respectively.

The increase in V_{oc} to values higher than that obtained on a chemically etched electrode (Table I) is a direct consequence of a decrease in cathodic dark current [4]. The observed increase in photocurrent after photoetching is mainly due to the removal of surface traps and consequent reduction in the surface recombination.

The results shown demonstrate that chemical etching is not sufficient to obtain reasonably defect-free surfaces, essential for obtaining satisfactory photo-output in PEC cells. Photoetching, in this context, is a technique to improve the output parameters.

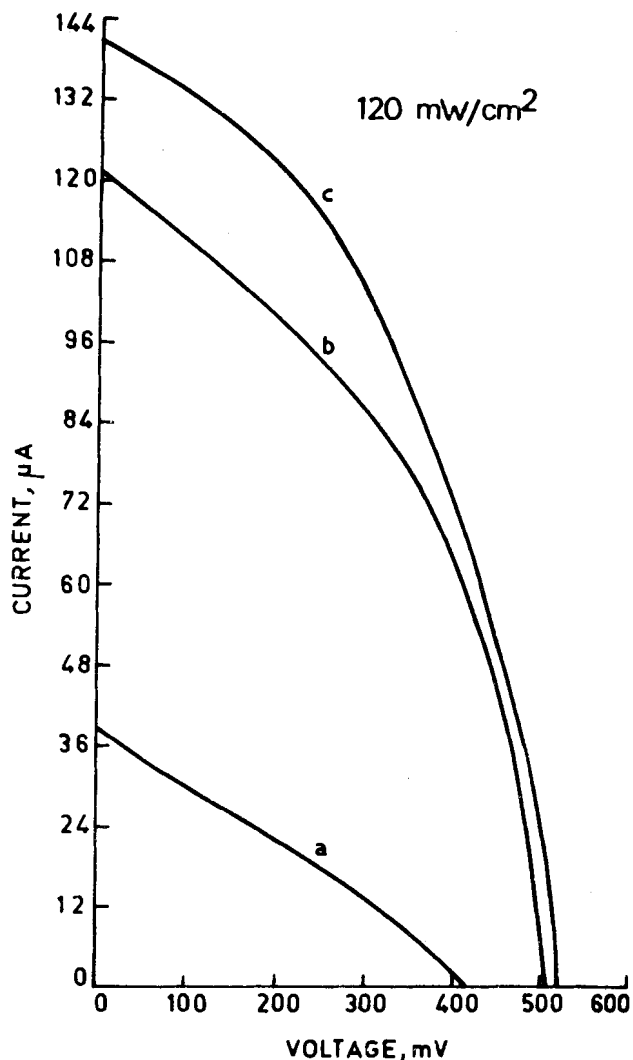


Fig.2: Current-voltage curves under 120 mW cm⁻² tungsten-halogen illumination. Curve a : Chemically etched electrode; Curve b : Immediately after photoetching (subsequent to chemical etch); Curve c : After 1 h of continuous illumination;

Table I: PEC cell parameters at 120 mW cm⁻² for chemically etched and photoetched CdS electrodes

Sl. No.	Surface treatment/experimental conditions	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	ff
1.	Chemical etch (conc.HCl, 30 sec)	410	0.64	0.28
2.	Photoetch (10 times diluted solution of 97% HCl and 3% HNO ₃ , 30 sec)	505	2.03	0.44
3.	After 1 hour illumination under short-circuit	520	2.33	0.42

CONCLUSION

Photoetching in a dilute acid solution enhances the photoresponse characteristics of a single crystal CdS electrode considerably in PEC cells.

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