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Electrochemical solar cell based on a sprayed CdS film photoanode

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Electrochemical studies of the CdS film deposited onto a transparent conductive SnO_2-coated glass slide by chemical spray deposition were performed in aqueous polysulphide solutions and the output characteristics of the electrochemical photocell (sprayed CdS film/polysulphide electrolyte/Pt) were measured. It was proved to be possible to construct a regenerative photocell free from the light losses through the polysulphide solution path by illuminating the CdS film anode through the SnO_2-coated glass. Quantum yield and the maximum energy conversion efficiency of this photocell for monochromatic excitation of 480 nm were about 8% and 0.5%, respectively. It is concluded that the poorer quantum yield of this photocell employing CdS film than that of a photocell employing single crystal CdS can be attributed to the existence of lattice imperfections in the film.

1. Introduction

Electrochemical solar cells based on the *n*-type cadmium chalcogenides and some III–V compounds, e.g., GaP, GaAs, and InP, in the chalcogenide/polychalcogenide redox electrolytes, have attracted much attention as practically possible solar energy convertors in the place of the TiO_2-electrochemical photocell [1–6]. The key findings are that chalcogenide or polychalcogenide ions enable those semiconductor materials to be photoelectrochemically stable and make the flat-band potential of those electrodes shift towards the cathodic direction. It has been also found that these photocells are regenerative ones in which the reduction of the polychalcogenide ion occurs at the cathode.

We have investigated the CdS/polysulphide anode system in an electrochemical solar cell and confirmed the above-mentioned facts [6]. It has been found, however, that light losses through the polysulphide solution path to the CdS electrode surface cannot be neglected, as the polysulphide solution absorbs the light with wavelength ranges of interest [1, 7].

In order to prevent these light losses, we have constructed the thin film CdS-based electrochemical solar cell which can be illuminated from the rear surface of the anode. The use of a thin film semiconductor anode may also help to reduce the inner resistance of the cell.

A chemical spray deposition technique was employed for the preparation of CdS thin film in this experiment from the practical viewpoint of a future realization of a large scale solar cell, since this technique enables us to prepare a large thin film by a rather simple operation [8–10]. Our preliminary results concerning the photoelectrochemical behaviour of the sprayed CdS film electrode have been already published [11]. In the present work, the polarization characteristics of these electrodes were investigated in more detail. The quantum yield and the energy conversion efficiency of an electrochemical solar cell using a sprayed CdS film anode as well as its performance characteristics were also discussed.

2. Experimental

2.1. *Preparation of sprayed CdS thin films*

The schematic diagram of the apparatus for chemical spray deposition of CdS thin films is given in Fig. 1. This apparatus consists of a device

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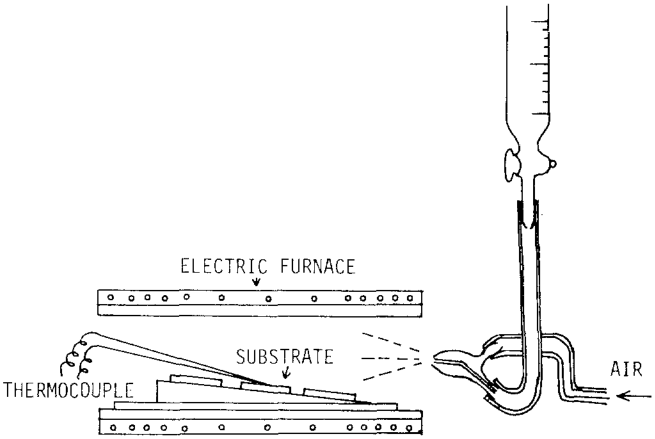

Fig. 1. Apparatus for chemical spray deposition of CdS thin film.

to atomize the spray solution and a substrate heater. The glass substrates, covered with a transparent conducting SnO_2 layer, were placed in an electric furnace and heated at a controlled temperature in the range of 250–350° C. Then the mixture of aqueous solutions of $CdCl_2$ (0·02 M) and thiourea (0·02 M) was sprayed onto these heated substrates (75 mm x 25 mm x 1 mm) through a nozzle from the spray bottle used for gas chromatography, as illustrated in Fig. 1. The spray operation was performed for 2 s repeatedly at regular intervals to allow the substrate temperature to recover after each spray operation. The volume of the spray solution was about 0·7 ml at every spray operation and the total volume to make a CdS film thickness of 100 nm was about 50 ml.

The grains of deposits thus obtained are irregular in shape and size, and neither a crack nor hole was observed by an electron microscope. X-ray diffraction peaks of most of these films are in accordance with those of pulverized CdS with hexagonal (wurtzite) structure. Sometimes a CdS film with cubic (zincblende) structure, which is stable below about 400° C, was also obtained, as shown in Fig. 2, when sprayed at a lower temperature.

The thickness of CdS films used for this photoelectrochemical study was about 200 nm. A copper wire was attached to one end of the conducting SnO_2-coated glass substrate with a silver epoxy.

2.2. *Electrochemical measurements*

The electrochemical photocell used in this work is depicted in Fig. 3. The polarization measurements of sprayed CdS thin film electrodes were performed by the potentiostatic method under illumination from the rear surface of the CdS film and current–potential curves were recorded with an $X–Y$ recorder. A standard three-electrode electrochemical cell with a platinized Pt electrode as a counter-electrode and a saturated calomel electrode as a reference electrode was used. The electrode potential always refers to this reference electrode. A 500 W Xe arc lamp was used as a light source and the spectral distribution of the photocurrent was determined by using a monochromator. The light intensity was measured with a calibrated thermopile placed at the same position as the working electrode. Current–voltage characteristics of the photocell shown in Fig. 3 were measured by varying the external load. Polysulphide solutions were prepared from sulphide solutions by the addition of sublimed sulphur.

3. Results and discussion

3.1. *Polarization behaviour*

Fig. 4 shows the typical polarization curves for a sprayed hexagonal CdS and cubic CdS film electrode in the dark and under illumination in an aqueous sulphide solution. The dark current in the potential region of $-1{\cdot}2 \sim 0$ V is essentially zero at both electrodes. There appeared a steep rise in anodic current at higher positive potentials. This current in the dark is probably due to electrons tunnelling in the conduction band of CdS. A significant photocurrent due to the photoanodic

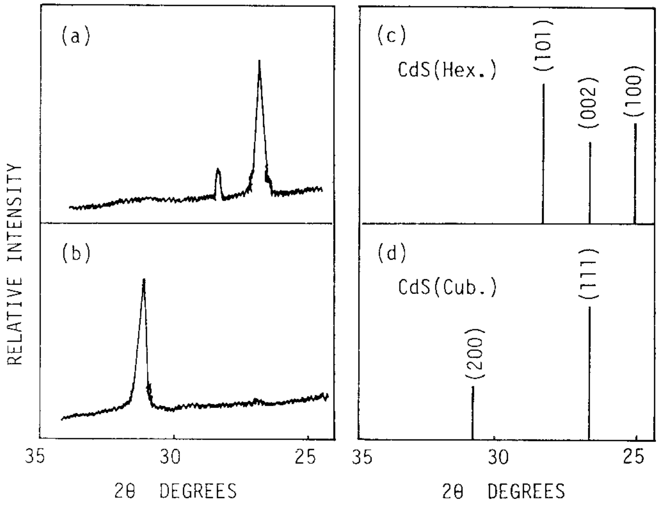

Fig. 2. X-ray diffraction profiles. (a), (b); Films as grown. (c), (d); ASTM data for pulverized CdS.

oxidation of the sulphide ion starts to flow above − 1·4 V and this photocurrent tends to saturate at higher anodic potentials. This photocurrent depends upon the intensity of the incident light with an energy equal to or higher than the band-gap of the CdS electrode. The photocurrent for a cubic CdS film electrode is about one-tenth of that for a hexagonal CdS film electrode. Thus hexagonal CdS film electrodes were used in subsequent experiments.

The spectral distribution of the photocurrent for a sprayed CdS film electrode compared to that for a single crystal CdS electrode is given in Fig. 5. No significant difference between the two kinds of CdS electrodes was observed. The spectral response of this film electrode under illumination through the SnO_2-coated glass was essentially identical in shape and wavelength region to that through the electrolyte in an aqueous sulphide solution.

A negligibly small anodic photocurrent was observed in the electrolyte containing 1 M S when the conventional type cell in which a CdS anode

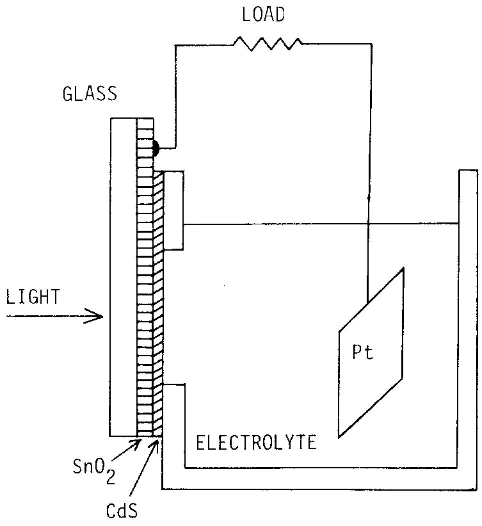

Fig. 3. Electrochemical photocell using sprayed CdS film.

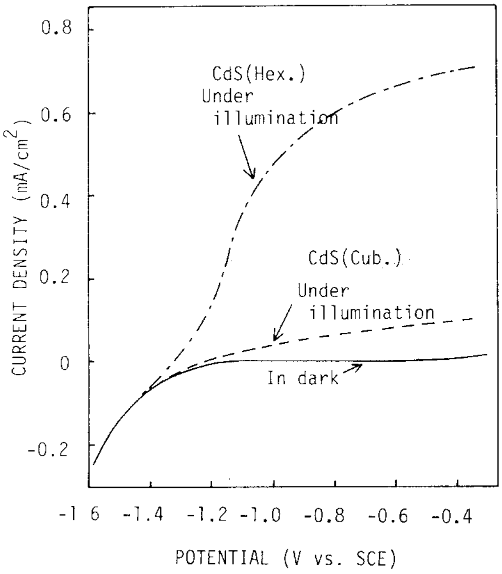

Fig. 4. Current–potential curves for sprayed CdS film electrodes in the dark and under illumination in 1 M NaOH +1 M Na_2S solution.

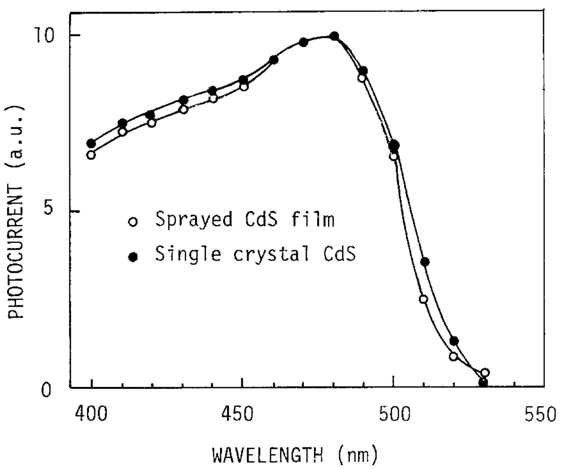

Fig. 5. Spectral distribution of anodic photocurrent at a potential of 0 V (versus SCE).

was illuminated through the electrolyte was used, since polysulphide solution considerably absorbs the light with wavelength ranges of interest for CdS [7]. The energy losses due to this light absorption can be prevented by the back illumination, as can be seen from Fig. 6. Anodic photocurrent values in both sulphide solution and polysulphide solution are almost the same, especially at higher positive potentials. The fact that the anodic photocurrent in the polysulphide solution is smaller than that in the sulphide solution below − 0·9 V may be due to the simultaneous occurrence of the reduction of polysulphide ion on the CdS electrode.

The cathodic onset potential of a Pt electrode in an aqueous polysulphide solution is more positive than that in an aqueous sulphide solution by about 0·3 V, indicating that the reduction of polysulphide ion takes place in preference to H_2 evolution. Fig. 6 suggests that the polysulphide solution is superior to the sulphide solution as the electrolyte for this CdS electrochemical photocell.

3.2. *Cell performances*

An example of the cell performances under white light of a Xe lamp is shown in Fig. 7. Both the open-circuit voltage and the short-circuit current are increased by the addition of sulphur into the sulphide solution, which is attributed to the shift of the rest potential of a Pt electrode towards the positive direction and, consequently, to the increase of the cathodic current, as can be expected from the results in Fig. 6. With the increase of the concentration of dissolved sulphur, the short-circuit current is increased. The open-

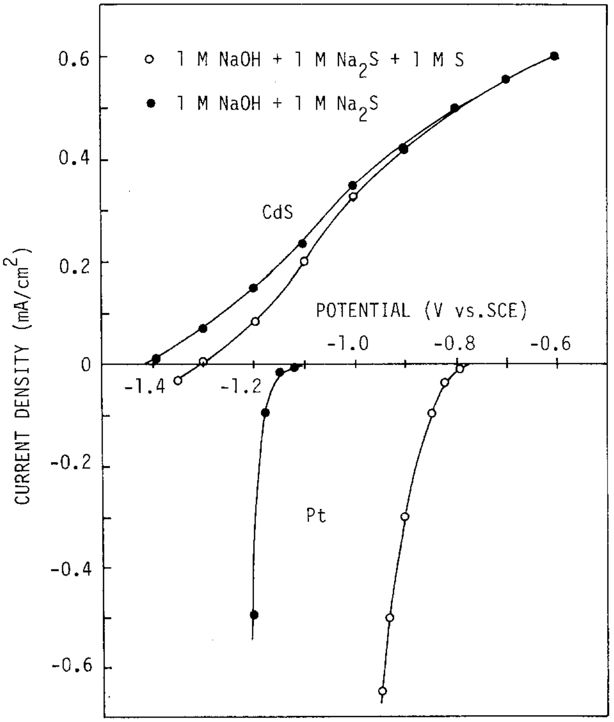

Fig. 6. Photoanodic polarization curves of sprayed CdS film electrode and cathodic polarization curves of Pt electrode in sulphide or polysulphide solution.

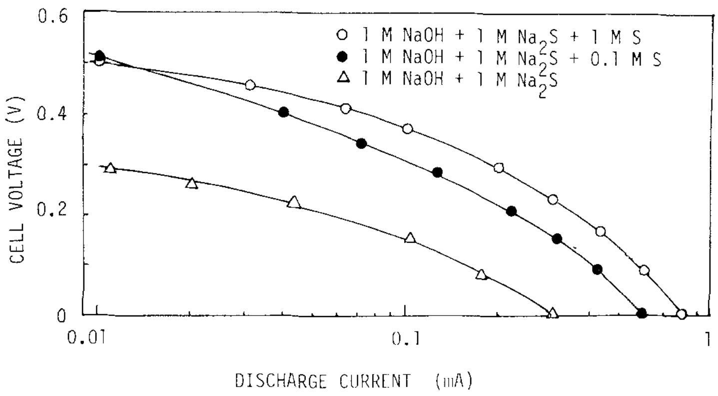

Fig. 7. Current–voltage curves for sprayed CdS/S^{2-} (or S$_x^{2-}$)-containing electrolyte/Pt photocell. Apparent surface area; 2 cm^2.

circuit voltage, however, cannot be increased so much, since the photopotential of the CdS anode as well as the potential of the Pt cathode is determined by the redox reaction of the sulphide/polysulphide couple.

Fig. 8 shows the short-circuit current–time curves for this electrochemical photocell. No evidence of dissolution and flaking-off of the CdS film photoanode was found after the passage of 15 C.

3.3. *Quantum yield*

Some representative output characteristics for this electrochemical photocell are given in Table 1. The wavelength of the light in this table is 480 nm. Fill factors of this cell were around 0·4. Quantum yields for the short-circuit current of this photocell are in the range 7 ~ 8% and maximum energy conversion efficiencies are about 0·5% for monochromatic excitation (480 nm) in these light intensity ranges. Wrighton *et al.* [12] have found, recently, that the electrochemical photocell based on the single crystal CdS in the sulphide/polysulphide redox electrolyte attains a maximum power conversion efficiency of 6·8% for monochromatic input power at a wavelength of 502 nm. It is necessary to improve these characteristics of our photocell using a polycrystalline CdS film photoanode.

Fig. 9 shows the electrode potential dependence of the quantum yield for a sprayed CdS film electrode under illumination of monochromatic light of wavelength 400 nm, 480 nm, and 520 nm. The photopotential of the CdS film anode under the short-circuit condition was −0·74 V under illumination of 480 nm monochromatic light. In the case of a single crystal CdS based cell, the quantum yield reaches about unity at this potential. Our sprayed polycrystal

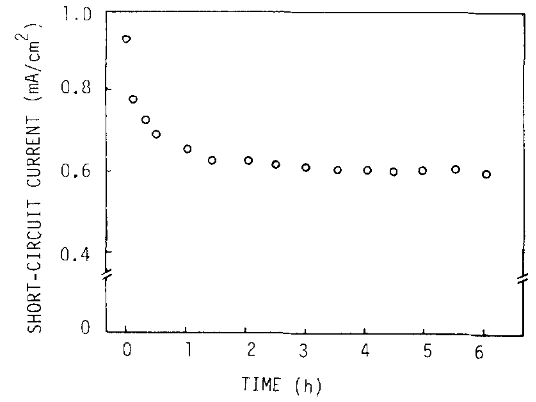

Fig. 8. Short-circuit current versus time for sprayed CdS/polysulphide electrolyte/Pt photocell.

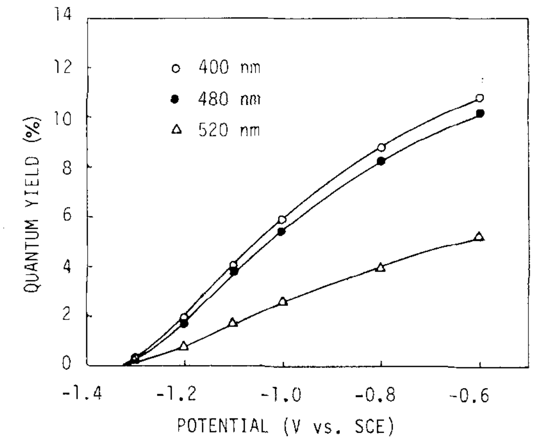

Fig. 9. Quantum yield–potential curves for sprayed CdS film electrode in 1 M NaOH + 1 M Na$_2$S + 1 M S solution.

Table 1. The quantum yields and the power efficiencies for the electrochemical photocell, sprayed CdS film/polysulphide electrolyte/Pt with 480 nm wavelength light

Light intensity (mW cm^{-2})	*Open-circuit voltage* (V_{oc}) (V)	*Short-circuit current* (I_{sc}) (μA cm^{-2})	*Maximum output power* (P_{max}) (μW cm^{-2})	*Fill factor*	η^* (%)	$\phi^\dagger_{max}$ (%)
0·31	0·30	8·8	1·1	0·42	7·3	0·35
0·40	0·31	12	1·6	0·43	7·7	0·40
0·59	0·31	19	2·7	0·42	8·3	0·46
1·29	0·38	42	5·9	0·37	8·4	0·46
1·60	0·40	52	7·6	0·37	8·4	0·48
2·30	0·42	72	11·7	0·39	8·1	0·51

* Quantum yield for electron flow at short-circuit
† Maximum power conversion efficiency

CdS film, however, shows 15% at best under higher anodic polarization.

Now, we have to discuss the reasons for such a poor quantum yield of this photocell. Two facts must first be mentioned in connection with this discussion. Firstly, all data are uncorrected for the losses of the light due to the reflection by the glass substrate and SnO_2 film. According to our measurements, these reflection losses are about 10% and 5% of the incident light, respectively. Secondly, we used the conducting SnO_2 film with about 85 ~ 90% transmission in the wavelength ranges of 400 ~ 520 nm. Moreover, we should point out the light losses due to transmission through the CdS film. Quantum yield should increase with the increase of film thickness, provided that the penetration depth of light is larger than the film thickness. The penetration depth of light is determined by the absorption coefficient α. According to our measurements, α is $10^4 \sim 10^5$ cm^{-1} in the wavelength range of 400–520 nm, which corresponds to 100 ~ 1000 nm for the penetration depth of light. As the thickness of CdS film used in this experiment was about 200 nm, the transmission loss of light can not be neglected.

The main reason for the poor quantum yield for this electrochemical photocell can be attributed to the recombination of photo-generated holes with electrons. In the case of the TiO_2 based electrochemical photocell, the difference between the anodic onset potential of the illuminated TiO_2 electrode, which nearly agrees with the flatband potential of this electrode, and the equilibrium potential of the H^+/H_2 redox couple is very small and the band bending in the TiO_2 electrode surface under operating conditions is so small that most photo-generated electron–hole pairs recombine [13]. Our result that the quantum yield is low even under higher anodic polarization indicates that the direct recombination losses are not so predominant but there may be a lot of recombination centres due to the lattice imperfections in the CdS film, e.g., poor crystallinity of the CdS film and the existence of impurities in the film. Thus the improvement of crystallinity of a sprayed CdS film is required in order to obtain a better quantum yield and output power of this electrochemical photocell. The crystallinity of sprayed CdS films should be influenced by substrate temperature during the spray operation and by the heat treatment of films. The effect of impurities remains unknown. Detailed results on these points will be discussed in a subsequent paper.

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