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ELECTROCHEMICAL PHOTOCELL USING SPRAYED CdS FILM ELECTRODE

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Photoelectrochemical studies of CdS film deposited by chemical spray deposition onto the glass substrate covered with a conducting SnO_2 layer were performed in aqueous sulfide or polysulfide solution. Similar behavior to that obtained with a single crystal or a sintered CdS electrode was observed. It is concluded that this sprayed CdS film electrode can be effectively used as the anode of the electrochemical photocell, CdS/aqueous polysulfide electrolyte/Pt, in which CdS anode is illuminated through SnO_2-coated glass.

Recently, the studies on the CdS-electrochemical photocell using sulfide/polysulfide redox system have been reported.1)-4) As CdS can be stabilized against photoanodic dissolution in this redox electrolyte, it is unnecessary to use a single crystal or a sintered CdS electrode as the anode of the electrochemical photocell. The use of a thin film electrode in the place of such an electrode would reduce the inner resistance of the photocell. Miller and Heller2) investigated an electrochemical photocell using a CdS film electrode formed by the anodization of Cd in aqueous sulfide solution. We have prepared CdS thin films by reactive DC or RF sputtering technique and investigated the photoelectrochemical behavior of these film electrodes. As these films often peel off from the substrate during polarization measurements, reproducible data have not been yet obtained. A CdS thin film prepared by chemical spray deposition shows better adhesion to the substrate. This technique has been used successfully for preparing conducting layers of SnO_2 and thin films of II-VI compounds such as CdS5) and ZnO.6) One of the principal advantages of this technique is that films with large surface area can be prepared easily. This is one of the most important points for realizing a large scale solar cell in the future.

In this paper, photoelectrochemical behavior of the sprayed CdS film electrode in aqueous sulfide or polysulfide solution was described. The application of this electrode to the electrochemical photocell was also discussed.

The CdS films were prepared on the glass substrate covered with a conducting SnO_2 layer. The substrates were placed in an electric furnace and heated at a controlled temperature in the range of 160-350°C. Then the mixture of aqueous solutions of $CdCl_2$ (0.02 mol/dm^3) and thiourea (0.02 mol/dm^3) was sprayed onto the substrate (75 mm × 25 mm × 1 mm) through a nozzle from the spray bottle used for gas chromatography. The spray operation was performed for 3 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 CdS film thickness of about 400 nm was 100 ml.

An electron micrograph of CdS film thus obtained is shown in Fig.1. The grains of deposits are irregular in shape and size and neither crack nor hole was observed. X-ray and electron diffraction analysis showed that these CdS films possessed a polycrystalline wurtzite structure. The thickness of CdS films used for this study was 200-400 nm. A copper wire was attached to one end of the conducting substate with a silver epoxy.

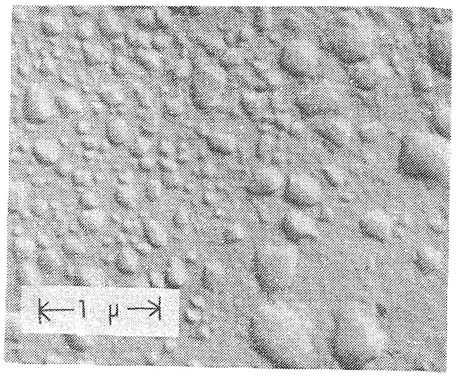

Fig.1 Electron micrograph of a sprayed CdS film

The electrochemical experiments were performed under potentiostatic conditions using a platinized Pt electrode as a counter electrode and a saturated calomel electrode as a reference electrode. A 500 W Xe lamp was used as a light source. The spectral distribution of the photocurrent was determined by using a monochromator.

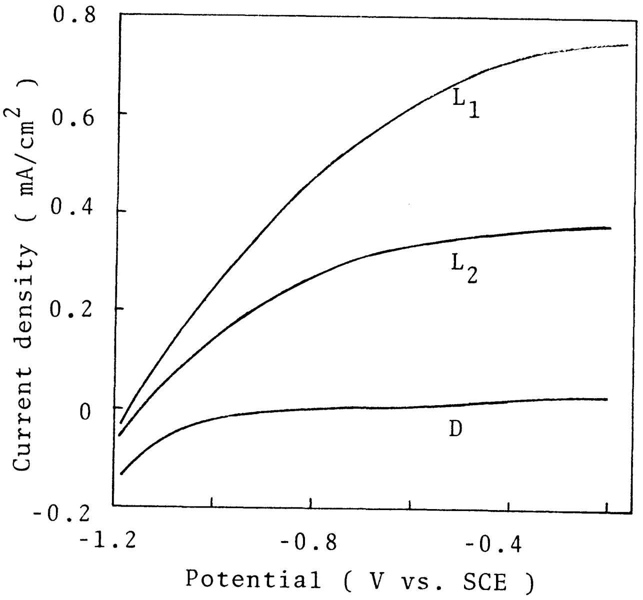

Fig.2 Current density - potential curves for a sprayed CdS film electrode in 1 mol/dm^3 NaOH + 1 mol/dm^3 Na$_2$S solution
D ; In dark
L$_1$, L$_2$; Under illumination
Light intensity ; L$_1$ = 2L$_2$
Sweep speed ; 0.033 V/s

Figure 2 shows the typical polarization curves for a sprayed CdS film electrode in dark and under illumination in aqueous sulfide solution. These curves are similar to those obtained with a sintered CdS electrode.3)4) A significant photocurrent flows under anodic polarization and this photocurrent reaches a saturated value at higher anodic potentials. This saturation current is proportional to the light intensity and the electrochemical reaction in this potential region is controlled by the supply of holes to the CdS electrode surface. This reaction is the photoanodic oxidation of S^{2-} ion, as have already been reported with a single crystal CdS electrode1) and a sintered CdS electrode.3)4)

On the other hand, very small current flows at 0 V (vs. SCE) in dark but the current rise occurs under higher anodic polarization. This is probably due to the tunnelling. The electrode process in this region was not investigated further in the present work.

Since the band gap of SnO_2 is considerably larger than that of CdS (SnO_2 ; 3.7 eV, CdS ; 2.4 eV), this system can be illuminated from the reverse side, i.e., through SnO_2-coated glass. The polarization curves under illumination through SnO_2-coated glass were similar to those shown in Fig.2. The magnitude of the photocurrent observed under illumination through SnO_2 was comparable to that observed under illumination through electrolyte. Significant difference in the spectral distribution of the photocurrent was not observed, which is different from the results obtained with TiO_2 film electrode prepared by CVD technique.[7)]

These sprayed CdS film electrodes did not peel off from the substrate even when these were used many times in polarization measurements and reproducible data could be obtained.

A polysulfide solution absorbs the visible light, which leads to the considerable loss in the conversion efficiency of the solar energy. This problem may be solved by using the electrolytic cell of the type shown in Fig.3. The polarization curves measured by using this electrolytic cell were shown in Fig.4.

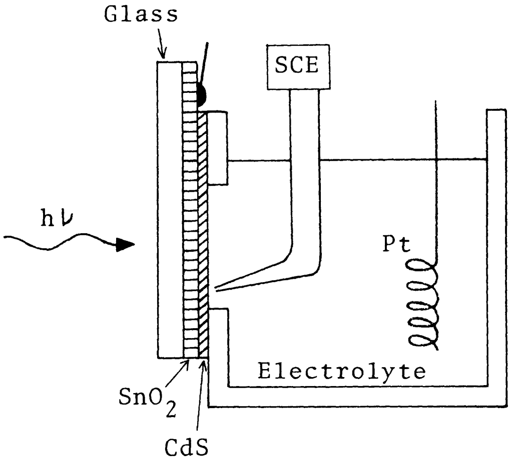

Fig.3 Schematic diagram of electrolytic cell for illumination through SnO_2

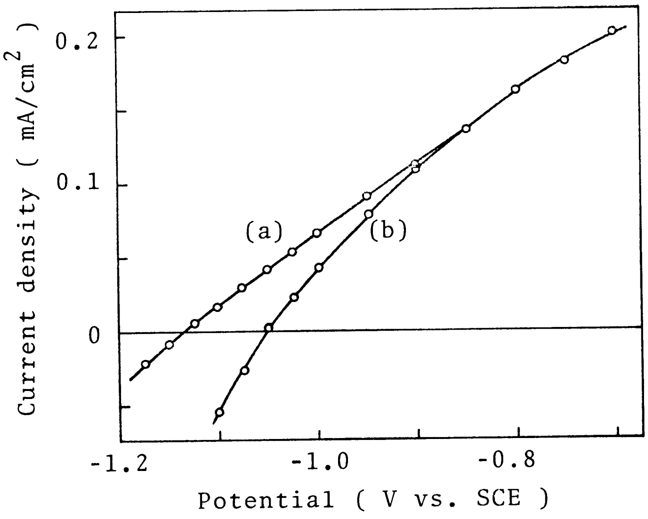

Fig.4 Current density - potential curves for a sprayed CdS film electrode under illumination

$\xrightarrow{h\nu}$ |glass|SnO_2|CdS|electrolyte

Electrolyte ;

(a) 1 mol/dm^3 NaOH + 1 mol/dm^3 Na_2S

(b) 1 mol/dm^3 NaOH + 1 mol/dm^3 Na_2S + 0.5 mol/dm^3 S

Anodic photocurrent values in both solutions are nearly the same at potentials above -0.9 V. The electrode potential at which the polarization current becomes zero in polysulfide solution is more positive than that in sulfide solution. This fact may be due to the simultaneous occurrence of the reduction of polysulfide ion in preference to H_2 evolution reaction on the CdS electrode in polysulfide solution.

On the other hand, cathodic onset potential of a Pt electrode in aqueous polysulfide solution (Electrolyte (b) in Fig.4) is more positive than that in aqueous sulfide solution (Electrolyte (a) in Fig. 4) by ca. 0.3 V, due to the occurrence of the reduction of polysulfide ion. These results indicate the predominance of using polysulfide solution as the electrolyte for a CdS-electrochemical photocell of this type.

Typical example of the cell performances under Xe lamp are shown in Fig.5.

It can be concluded from the experimental results mentioned above that the CdS film deposited onto the glass substrate covered with a conducting SnO_2 layer by chemical spray deposition technique can be effectively used as the anode of the electrochemical photocell, CdS/aqueous polysulfide electrolyte/Pt, in which CdS anode is illuminated through the SnO_2-coated glass.

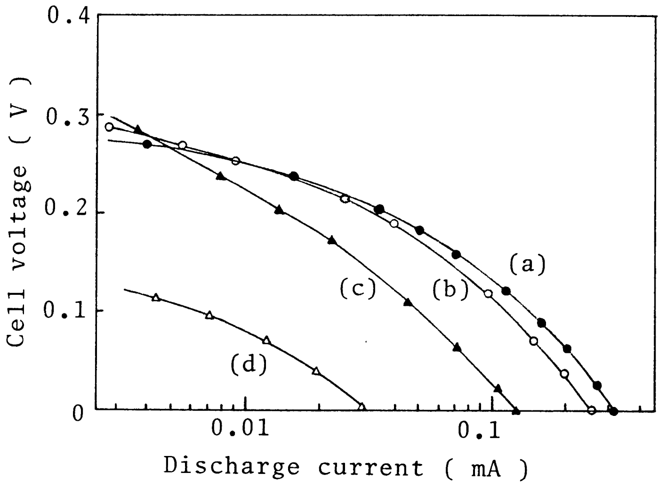

Fig.5 Cell performances for the electrochemical photocell, sprayed CdS film/sulfide or polysulfide electrolyte/Pt

$h\nu$ → |glass| SnO_2 | CdS | electrolyte

Electrolyte ;

(a) 1 mol/dm^3 NaOH + 1 mol/dm^3 Na_2S + 1 mol/dm^3 S
(b) 1 mol/dm^3 NaOH + 1 mol/dm^3 Na_2S +
+ 0.5 mol/dm^3 S
(c) 1 mol/dm^3 NaOH + 1 mol/dm^3 Na_2S
+ 0.1 mol/dm^3 S
(d) 1 mol/dm^3 NaOH + 1 mol/dm^3 Na_2S

Apparent surface area ;
CdS anode; 2 cm^2 , Pt cathode; 1.7 cm^2

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