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Decrease in the Quantum Efficiency of a Cadmium Sulfide Photoanode Due to Sulfur Deposition. Determination of Quantum Efficiency by Temperature Measurement

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CdS photoelectrodes dissolve during photoanode reactions in a supporting electrolyte solution, and the quantum efficiency changes due to sulfur deposition. Temperature measurement technique has been used in this work to determine the quantum efficiency of the CdS photoelectrode. It has been found that decreases in the quantum efficiency can be monitored easily by this method.

A number of photoelectrochemical cells based on semiconductor electrodes for the purpose of converting solar energy either to chemical energy (*e.g.* the photodeomposition of water) or to electrical energy have been reported.[1–3] Most investigations to date have focused on the more familiar semiconductor compounds, *e.g.* Si, GaAs, GaP, ZnO, CdS, and TiO_2. Stable electrodes, such as TiO_2, have a large bandgap $Eg \geqslant 3\,eV$, while materials with a smaller bandgap, such as CdS, tend to be unstable.

In the case of a CdS photocell, the electrode itself can be oxidized by photogenerated positive holes, so that the Cd^{2+} ions dissolve into the solution and atomic sulfur is deposited onto the electrode surface.[4] Hence, the photocurrent and the quantum efficiency of the electrochemical photocell dacay rapidly with time due to the filtering effect of the deposited sulfur.

The energy conversion efficiencies and quantum effiiencies of electrochemical photocells are very important factors in the effective utilization of solar energy. Recently Fujishima *et al.*[5] used a new method to measure the temperature change on a semiconductor electrode during photoelectrochemical reaction for determining the intrinsic quantum efficiency of the photoelectrochemical cell. When the semiconductor electrode is illuminated with a monochromatic light pulse having an energy E, with an average absorbed intensity I for a time t, consideration of the energy balance within the semiconductor photoelectrode in the limiting photocurrent region will result in the equation:

$$E\frac{\Delta T}{\Delta T^{\circ}} = \frac{Q_{sc}+T\Delta S}{It} + \eta e(V-V_{fb}), \tag{1}$$

where ΔT is temperature change of the semiconductor surface; ΔT°, temperature change of the semiconductor surface in the open circuit; ΔS, entropy change for the semiconductor electrode reaction; Q_{sc}, heat evolved in the semiconductor *via* recombination and radiationless processes; η, quantum efficiency of photoelectrode reaction; V, applied potential *vs.* reference electrode; V_{fb}, flatband potential *vs.* reference electrode.

Therefore, under constant conditions of illumination (*i.e.* EIt held constant) a plot of $E\frac{\Delta T}{\Delta T^{\circ}}$ against $(V-V_{fb})$[5,6] yields the quantum efficiency η from the slope of the straight line and the loss term, $(Q_{sc}+T\Delta S)/It$, is obtained from the intercept of the $E\frac{\Delta T}{\Delta T^{\circ}}$ axis at $V=V_{fb}$.

To understand the quantum efficiency obtained from the relationship between temperature change and applied potential, two model cases are shown in Fig. 1. When $\eta=1.0$ the slope of $E\frac{\Delta T}{\Delta T^{\circ}}$ against V should be 1.0, since all the electrons excited into the conduction band by light irradiation move from the surface into the bulk of the semiconductor through the space charge layer generating heat. When $\eta=0.5$, the slope should be 0.5, since half of the excited electrons are recombined with the holes in the surface region.

In this study we used this method for measuring the change in the quantum efficiency of the photoelectrochemical reaction of the CdS photocell because of its great simplicity and the fact that there is no need to count the number of photons irradiated and/or absorbed.

Experimental

Electrode Preparation. The resistivity of the *n*-CdS single crystal used was 0.4 Ω cm, and the carrier concentration was $6\times10^{16}\,cm^{-3}$. The ohmic contact was made by rubbing In-Ga alloy on the back surface of the crystal and then attaching a copper wire to the contact with conducting Ag epoxy. The back and sides of the crystal were insulated and mounted on a flat piece of glass attached to a glass rod with epoxy resin.

Thermistors (Shibaura Electronics, Model BSB4-41A; nominal resistance 4 kΩ, sensitivity 0.052 °C/Ω), having a time constant 0.4 s when immersed in still water were used in matched pairs, in a differential arrangement with one held against the front surface of the semiconductor electrode and the other placed behind the electrode but not touching it.[5] The cell was carefully positioned so that the monochromatic light beam struck the electrode but none of the thermistors.

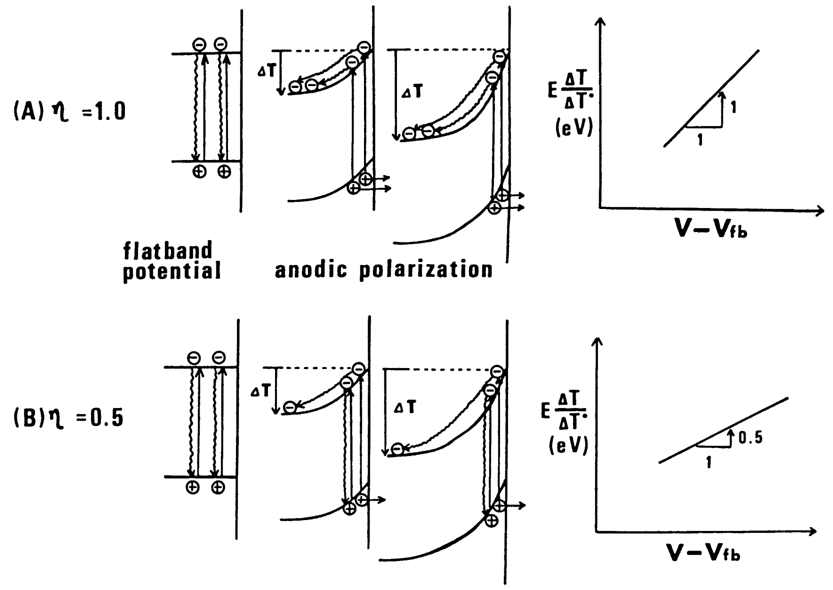

Fig. 1. Theoretical behavior of temperature change *vs.* potential.

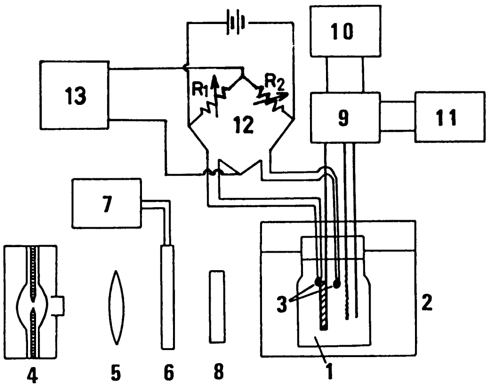

Fig. 2. Experimental apparatus.
1: cell, 2: water bath, 3: thermistor, 4: 500 W Hg lamp, 5: lens, 6: shutter, 7: timer, 8: filter, 9: potentiostat, 10: potential sweeper, 11: X-Y recorder, 12: D.C. bridge, 13: polyrecorder.

The CdS electrode was polished with sandpaper and etched for 10 s in concentrated HCl prior to use.

Apparatus. Figure 2 shows a block diagram of the experimental apparatus. The light source used was a 500 W Xenon lamp (Type SQ500) in an Ushio Model UI-501C lamp housing. Other apparatus included a lens to focus the light beam, a shutter to fix the irradiation period, and an interference filter (Koshin Kogaku) to select the wavelength of the exciting light.

Current-potential and current-time curves were measured under potentiostatic conditions with a Type HDV-7 potentiostat and Type KS-1 single scanner. These curves were displayed on an X-Y recorder (Type L23-24).

The electrochemical cell was a conventional three-electrode cell with a saturated calomel electrode (SCE) as the reference electrode and a Pt plate counter electrode.

All chemicals were of reagent grade and used without further purification.

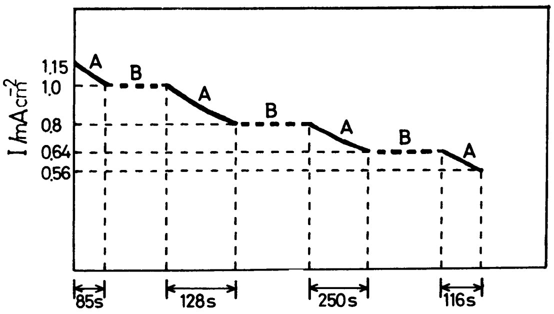

Fig. 3. Illustration of the experiment procedure.
A: Decrease of photocurrent in 0.2 M Na_2SO_4. B: Measurement of photothermal response in 0.1 M Na_2SO_3–0.2 M Na_2SO_4.

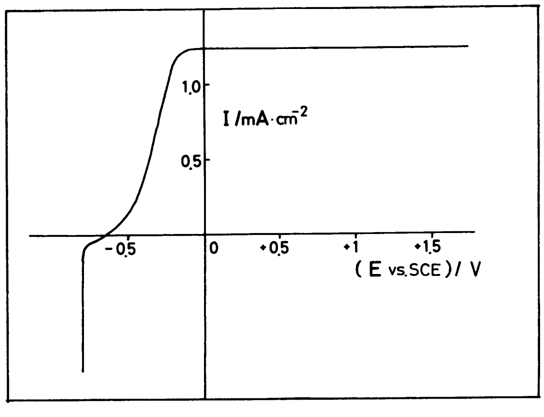

Fig. 4. Photocurrent *vs.* potential of CdS single crystal electrode in 0.1 M Na_2SO_3–0.2 M Na_2SO_4.

Procedure. Figure 3 shows the experimental procedure. A photothermal experiment on surface-fresh *n*-CdS photoelectrode in 0.1 M Na_2SO_3–0.2 M Na_2SO_4 (1 M=

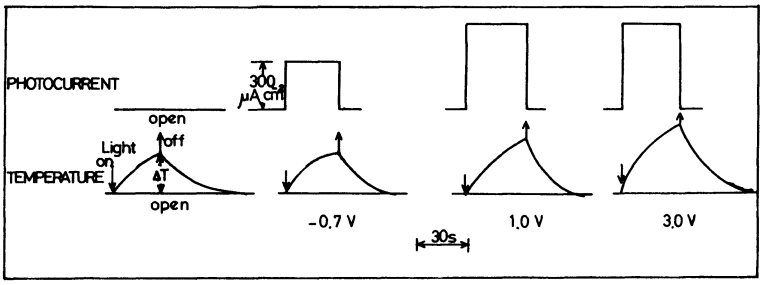

Fig. 5. Change in temperature *vs.* time (bottom) and anodic photocurrent *vs.* time (top) of the CdS anode in 0.1 M Na_2SO_3–0.2 M Na_2SO_4.

1 mol dm^{-3}) was first carried out according to the method reported.[5] The photothermal response and the saturated photocurrent, 1.15 mA/cm^2, were obtained. Then the electrode was put in 0.2 M Na_2SO_4 and the current-time was measured. The photocurrent gradually decreased because of sulfur deposition on the surface of the photoelectrode, and when it had decreased to a certain value (*e.g.* 1.0 mA/cm^2), the experiment was stopped. The electrode was immediately replaced in the 0.1 M Na_2SO_3–0.2 M Na_2SO_4 and the corresponding photothermal response was obtained. After that, the experiment was carried out alternately in the two solutions until the saturated photocurrent decreased to the lowest value in the experiment (*e.g.* 0.55 mA/cm^2).

Results are given for monochromatic irradiation at wavelengths shorter than that corresponding to the bandgap energy (*e.g.* 480 nm for CdS). Photothermal responses were obtained for the photoelectrode during anodic polarization, and under open circuit conditions in the electrolyte solutions. A change in temperature of the electrode caused a resistive change in the thermistor and produced a voltage imbalance in the DC bridge. The corresponding current and temperature changes were then plotted as a function of applied potential.

Results and Discussion

Figure 4 shows the current-potential characteristics of the CdS single crystal photoanode by using the 480 nm interference filter in 0.1 M Na_2SO_3–0.2 M Na_2SO_4 solution. In the dark, anodic photocurrent does not appear, but under illumination it does. The onset potential of the anodic photocurrent corresponds to the flatband potential of the photoanode, −0.75 V. The saturated photocurrent is stabilized at about 1.2 mA/cm^2.

The quantum efficiency of the CdS electrode was determined by temperature measurement in 0.1 M Na_2SO_3–0.2 M Na_2SO_4. Figure 5 shows the time dependency of changes in photocurrent and temperature of the CdS photoanode at each applied potential. Temperature increased when the light was turned on, and decreased when it was turned off. The relationship of temperature changes to applied potential is given in Fig. 6. The slope for CdS without deposited sulfur in the saturated photocurrent regions was approximately 1, nearly the same as reported by Maeda *et al.*,[6] but the slope decreased as sulfur was deposited on the electrode surface. In the absence of the reducing agent (Na_2SO_3) in the electrolyte solution (0.2 M Na_2SO_4), the photocurrent at the CdS photoanode resulted in the decomposition of the CdS according to the equation,[7]

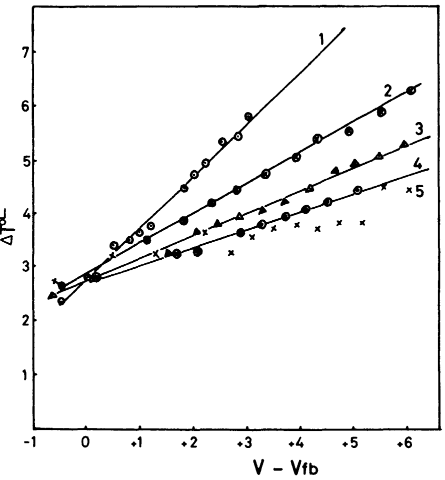

Fig. 6. Temperature change *vs.* potential of CdS single crystal electrode.
1: On fresh surface, 2—5: On surfaces with varying amounts of sulfur deposition. The photocurrents were observed in Na_2SO_3 solution. Therefore their values were almost constant as shown in dotted lines in Fig. 3; 1: 1.29(mA/cm^2), 2: 0.77, 3: 0.49, 4: 0.46, 5: 0.2—0.3

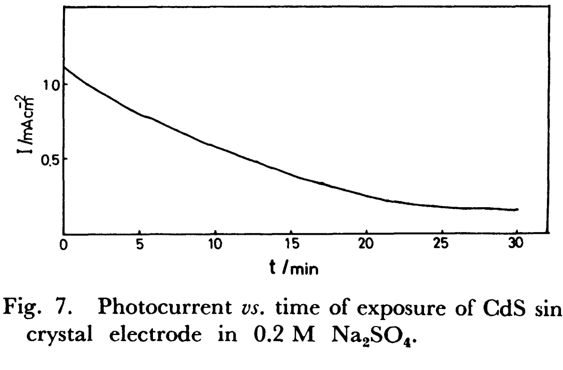

Fig. 7. Photocurrent *vs.* time of exposure of CdS single crystal electrode in 0.2 M Na_2SO_4.

$$CdS + 2p^+ \longrightarrow Cd^{2+} + S$$

and sulfur was deposited on the surface of the photoanode. Because the sulfur layer absorbed light, the intensity of the light penetrating it to impinge on the CdS single crystal decreased, so that the saturated photocurrent was reduced. The photocurrent decreased with the amount of sulfur, and with the time of

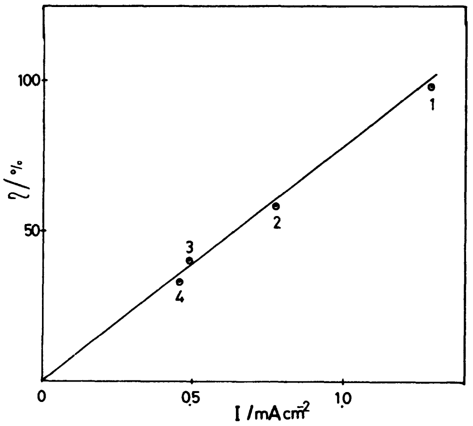

Fig. 8. Quantum efficiency *vs.* photocurrent of the CdS single crystal electrode. Number 1—4 was the same as Fig. 6.

exposure as shown in Fig. 7. Thus the saturated photocurrent corresponds to the amount of deposited sulfur. As the CdS photoanode decomposed in 0.2 M Na_2SO_4 to produce varying amounts of sulfur, a family of $E\frac{\Delta T}{\Delta T^\circ}$ *vs.* potential curves may be plotted (see Fig. 6). These lines corresponding to the amounts of sulfur deposited, remained linear in the saturated photocurrent regions, but their slopes varied with photocurrent. However, it was found at curve 5 in Fig. 6 that points at 0.35 mA did not form a straight line. Moreover, the saturated photocurrent increased during temperature measurement from 0.35 mA to 0.50 mA. It is suggested that in this case the deposited sulfur may not have adhered so strongly to the CdS surface, or may have broken off in part. A plot was made of slope, *i.e.*, quantum efficiency η, *vs.* photocurrent i, and it was found that η was also linear with i, as shown in Fig. 8. We assumed that it was the absorption of light by the deposited sulfur that resulted in the change of slope, since if the deposition layer was reflective, as for the reason of decrease of photocurrent, the slope would have been constant.

If the deposition layer adheres fully to the electrode surface, the amount of deposited sulfur, and presumably the average thickness of deposition layer will, in accordance with Faraday's law, be proportional to the number of coulombs. Therefore, the quantum efficiency of photocurrent will decreare with the number of coulombs flowed for surfur deposition. Actually we observed the decrease of quantum efficiency with the charge flowed for sulfur deposition.

This experiment indicates that the temperature measurement is also applicable to CdS photoanode on which sulfur is deposited.

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