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CATHODIC PHOTO-EFFECT AT CdS ELECTRODE IN AQUEOUS POLYSULFIDE SOLUTION

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In an aqueous polysulfide solution, a remarkable cathodic photocurrent was observed on the $(000\bar{1})$ face of a single crystal CdS electrode in addition to the usual anodic photocurrent. It can be presumed that this cathodic photocurrent is due to the reduction of polysulfide ion by the photo-generated electron and is associated with the presence of the surface states which are in the forbidden gap of CdS.

It has been reported1)-4) that an aqueous sulfide or polysulfide solution can be effectively used as the electrolyte for a CdS-electrochemical solar cell. The electrode reactions of this cell are the photoanodic oxidation of sulfide or polysulfide ion at a CdS anode and the reduction of polysulfide ion at a cathode, e.g., Pt electrode. It is generally well-known that in the case of n-type semiconductor electrode the photo-effect is observed only under anodic polarization. We have found that a CdS electrode shows not only such an anodic photo-effect but also an interesting cathodic photo-effect in an aqueous polysulfide solution. In this paper, the important results are described.

A commercial single crystal CdS with optically flat (0001) or $(000\bar{1})$ face was used as the working electrode. It has a resistivity of about 1 Ωcm and a donor concentration of 2.0×10^{16} cm^{-3}. Distinction between the (0001) face and the $(000\bar{1})$

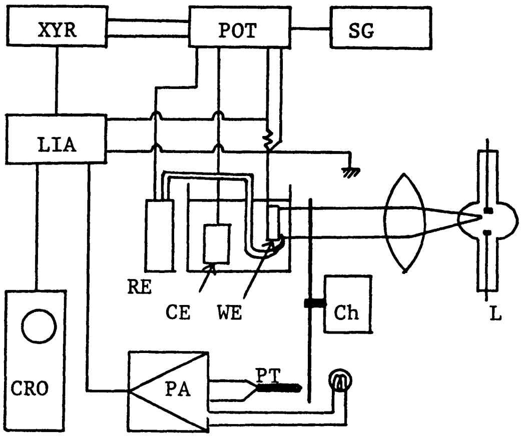

Fig.1 Block diagram of the experimental set-up for ac photocurrent measurement
POT; Potentiostat, SG; Sweep generator, LIA; Lock-in amplifier, Ch; Chopper, CRO; Oscilloscope, L; Light source (Xe lamp), PA; Pre-amplifier, XYR; X-Y recorder, PT; Photo transistor, WE; Working electrode, CE; Counter electrode, RE; Reference electrode

face was made by chemical etching.[5)] Good electrical ohmic contact of the CdS electrode with Cu wire was ensured by vacuum evaporated indium on the CdS surface. Prior to the measurements, the electrode was etched for 10 s in concentrated HCl and then rapidly washed with distilled water.

The electrochemical measurements were performed in an aqueous sulfide or polysulfide solution under potentiostatic conditions using a platinized Pt electrode as a counter electrode and a saturated calomel electrode as a reference electrode. The electrode potential always refers to this reference electrode. A 500 W Xe lamp was used as a light source. The light was chopped and the corresponding photocurrent was amplified by a lock-in amplifier and recorded on an X-Y recorder. This experimental apparatus is shown in a block diagram in Fig.1. The photocurrent thus obtained will be called "ac photocurrent" in this paper. The spectral response of the ac photocurrent was determined by using a monochromator. A polysulfide solution was prepared by the addition of sublimed sulfur to 1 M NaOH + 1 M Na_2S solution.

Cathodic polarization curves for the single crystal CdS electrodes in an aqueous sulfide or polysulfide solution are shown in Fig.2. The cathodic current of the $(000\bar{1})$ face (sulfur face) electrode at potentials under -1.3 V was increased by the addition of sulfur to a sulfide solution, indicating that this increased current was due to the cathodic reduction of polysulfide ions in the solution. On the (0001) face (cadmium face) electrode, on the other hand, the cathodic current is little affected by the addition of sulfur.

Figure 3 shows ac photocurrent - potential curves for the CdS electrode in an aqueous polysulfide solution. On the (0001) face electrode no cathodic photocurrent flows, whereas on the $(000\bar{1})$ face electrode a remarkable cathodic photocurrent appears and it exihibits the well-formed peak at about -1.6 V. The cathodic photocurrent flows on the $(000\bar{1})$ face electrode in the potential ranges where the reduction of polysulfide ions took place. It seems likely, therefore, that illumination en-

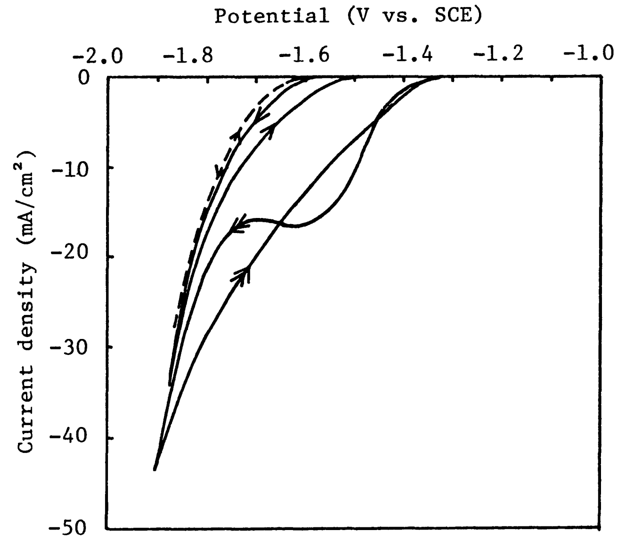

Fig.2 Cathodic polarization curves for single crystal CdS electrode in 1 M NaOH + 1 M Na_2S solution and 1 M NaOH + 1 M Na_2S + 1 M S solution

-->-- (0001) face and $(000\bar{1})$ face in sulfide solution

—>— (0001) face in polysulfide solution

—>>— $(000\bar{1})$ face in polysulfide solution

Sweep speed; 0.67 V/min

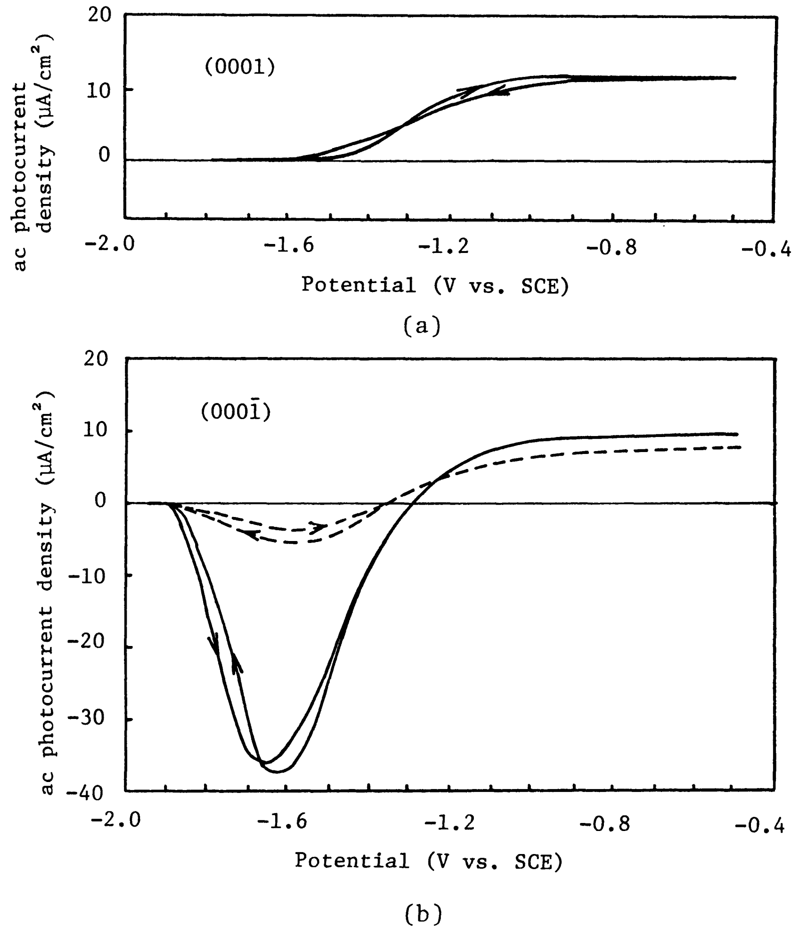

Fig.3 ac photocurrent - potential curves for (a) (0001) face and (b) (000$\bar{1}$) face of a single crystal CdS electrode in 1 M NaOH + 1 M Na_2S + 1 M S solution
Chopping frequency;
—— 30 Hz
---- 450 Hz
Sweep speed; 0.67 V/min

hances the rate of this electrochemical process.

The zero photocurrent potential where the value of the cathodic photocurrent becomes equal to that of the anodic photocurrent was about -1.3 V in the solution containing 1 M of dissolved sulfur, when the light was chopped at the frequency of 30 Hz. The cathodic photocurrent as well as the anodic photocurrent was increased nearly linearly with the increase of the light intensity. Thus the zero photocurrent potential is almost independent of the light intensity. It can be assumed, therefore, that the rate of the photocathodic reduction of polysulfide ions is controlled by the supply of electrons, majority carrier.

With the increase of the chopping frequency, the cathodic photocurrent was reduced compared with the anodic one, as shown in Fig. 3 (b). This means that the response for the cathodic photocurrent is slower than that for the anodic one. This relaxation process in the cathodic photo-effect may be associated with the presence of the surface states which are within the forbidden gap of CdS. That is, the photocathodic process seems to occur via the surface states. Similar results have recently been reported for TiO_2 6) and $SrTiO_3$ 7) electrodes. In the case of these oxide semiconductor electrodes, the energy level of the surface state is associated with the redox level of the O_2/OH^- couple in the solution. For a CdS electrode, this seems to be associated with the redox level of the S^{2-}/S_x^{2-} ($x \geqq 2$) couple.

Sulfur atom at the (000$\bar{1}$) face of CdS has a dangling bond with two electrons, whereas cadmium atom at the (0001) face of CdS has no electron dangling bond. Taking into account this fact, it can be presumed that the surface states mentioned above are induced by the interaction of these dangling electrons on the (000$\bar{1}$) face of CdS electrode with polysulfide ions.

On polarizing the electrode beyond -1.7 V, the hydrogen evolution and/or the cathodic decomposition of the CdS electrode should occur. It has already been reported[8)] that the rate of the latter is strongly influenced by illumination, whereas the former is not in KCl solution. Actually, the cathodic photocurrent passes a maximum at about -1.6 V and decreases down to zero at about -1.9 V, and while the CdS electrode is under cathodic polarization at potentials under -1.7 V, one can observe gases evolving from the CdS electrode surface. Then the steep rise of cathodic current around -1.7 V as shown in Fig.2 may be attributed to the hydrogen evolution.

The mechanism of the photocathodic reduction process will be discussed in more detail in a subsequent paper.

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