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Indium hexacyanoferrate(III) coating for stabilizing polycrystalline CdSe photoelectrodes

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Films of polycrystalline *n*-CdSe were prepared onto titanium substrates by electrodeposition from an aqueous bath. The materials were studied as photoelectrodes in a photoelectrochemical cell, using $Fe(CN)_6^{3-/4-}$ as redox couple. The CdSe electrode deteriorated within less than one hour due to photocorrosion. Depositing a thin coating of indium hexacyanoferrate(III) caused relatively small effects on parameters like conversion efficiency and fill factor, but increased the photostability dramatically, with no sign of decrease in cell current over 10 h.

1. Introduction

Cadmium selenide is an attractive candidate as photoelectrode for a photoelectrochemical (PEC) cell for conversion of solar energy into electricity, one reason being a band-gap (1.7 eV) near the optimum size for terrestrial application. A major problem for CdSe, as for all covalent semiconductors, is the tendency to photodecomposition, *e.g.* according to the reaction

$$CdSe + 2h^+ \longrightarrow Cd^{2+} + Se^0 \qquad (1)$$

One way to overcome this is by addition of a polysulphide redox couple to the solution [1–3], causing formation of a Cd–Se–S layer on the semiconductor surface, inhibiting further photocorrosion. However, the conversion efficiency of such a cell is low due to the strong light absorption of polysulphide in the visible region. Possible non-absorbing redox systems include the hexacyanoferrate (ferro/ferricyanide) redox couple [4, 5], which however is only partly stabilizing. Ways to overcome the remaining photocorrosion include the use of nonaqueous electrolyte solutions [6], and various protective coatings like conducting polymers.

A partly protective layer may also form spontaneously from corrosion products. Frese [8] found that the selenium layer obtained by photoetching of CdSe partially stabilizes the electrode against further photocorrosion, and also that the Se layer behaves as a good hole conductor. Another overlayer formation was reported by Rubin *et al.* [9]. They found that cadmium ions in the solution generated by photocorrosion of CdS [9] and CdSe [10] react with hexacyanoferrate ions to precipitate an insoluble $K_xCd_yFe(CN)_6$ surface coating partly inhibiting further photodecomposition of the electrode.

In searching for alternative coating materials we observed a study by Kulesza and Faszynska [11] on indium(III) hexacyanoferrate(II) overlayers formed by electrodeposition on glassy carbon, on metals, etc., which they found to be highly electroactive. It occurred to us that it also could be useful to protect a semiconductor against photocorrosion, as an inorganic analogue to an organic conducting polymer.

Any large scale application of semiconductors to solar energy conversion has to rely on polycrystalline materials in the form of thin films, and it is important to investigate not only single crystals but also polycrystalline semiconductors in PEC cells. Several ways of producing thin CdSe films are available, including electrodeposition [2]. Recently Gutiérrez and Ortega [12] published a study of the PEC properties of such films in the hexacyanoferrate system.

In the present paper we report preparation of polycrystalline *n*-CdSe films on a titanium substrate, its characteristics as photoanode in a PEC cell using hexacyanoferrate as redox couple, and the effects of a protective overlayer of indium ferrocyanide.

2. Experimental details

2.1. *Preparation of CdSe electrodes*

The CdSe electrodes were prepared in our laboratory by electrodeposition of CdSe on titanium rod (99.7%), using a modification of the procedure described by Hodes and coworkers [2]. The surface of Ti was carefully abraded (polished) with No. 1000 emery paper and etched in an aqueous HF solution (1 : 1) for a few seconds. The etching procedure was found to give improved adhesion of the deposit, better coverage of micropores, and improved grain growth. The electrolytic bath was an aqueous solution of 0.5 M KCl, 0.08 M $CdSO_4$ and 0.5 mM SeO_2, with pH adjusted with H_2SO_4 to pH 2. The anode was a cadmium rod suspended in the electrolyte and externally shorted to the titanium substrate. The plating was carried out with current densities $\sim 1.5\,mA\,cm^{-2}$, at room temperature and with stirring. Typically the electrolysis time was 40 min.

The electrodeposited films were annealed at 550° C. The electrodes were mounted on a brass shaft with silver epoxy. Finally, the assembly, with the exception for a 0.07 cm^2 CdSe surface, was encased in silicon rubber.

The deposition of CdSe is influenced by many factors, such as temperature, stirring conditions, current density, deposition time, surface pretreatment etc, and it is difficult to keep all these identical in all preparations. Only electrodes with microscopically homogeneous CdSe deposit surface, and showing a 'normal' current-voltage response, were used for subsequent experiments.

2.2. *Electrochemistry*

All experiments were performed under a nitrogen blanket and at room temperature. The electrolyte solution was flushed free of oxygen with pure nitrogen for 30 min before the electrode was immersed.

Linear voltammograms were carried out in a conventional three-electrode cell, using a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat. All potentials herein are referred to a saturated calomel electrode (SCE) used as reference electrode. A platinum gauze served as the counter electrode.

The same setup was used in our electrode coating procedure. The semiconductor electrode was etched with 6 M HCl for 10 s and placed in a freshly prepared solution containing 0.5 mM $InCl_3$, 0.5 mM $K_3Fe(CN)_6$ and 0.5 M KCl with pH adjusted to 2 with HCl. The system was kept in the dark at -250 mV for several minutes (typically 15 min).

2.3. *Photoelectrochemistry*

The light source was a Melles Griot 5 mW HeNe laser with a collimator. The light intensity at the surface of the photoelectrode was 4.5 mW cm^{-2}. Photocurrent–photovoltage curves were obtained in a two-electrode cell with an external resistance box and two multimeters. For long time *stability* measurements the resistance was chosen to give maximum output power of the cell (the working point), and a microcomputer (CBM128) was used for data acquisition and storage. Using the three-electrode arrangements, transient photocurrents at onset of illumination were measured for a series of potentials, using a BBC M 6011 digital oscilloscope. The *flat band potential* was taken as that potential below which no initial photocurrent could be observed. The value obtained (-700 mV) agrees well with literature data [13].

ATR FT-IR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy) measurements were performed using Perkin Elmer type 1800 spectrophotometer.

3. Results

Figure 1 shows a linear voltammogram of a CdSe cell in the dark, for potentials from $+240$ to -250 mV, and in absence and presence of hexacyanoferrate(III) in the electrolyte. In the former case, no electrochemical reactions are observed in this potential region. In the latter case, there is a cathodic process below -100 mV, indicating the reaction

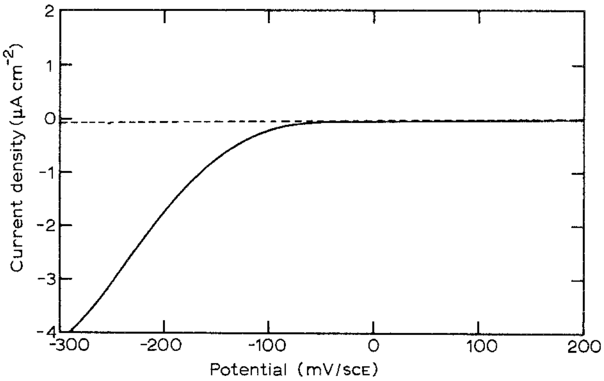

Fig. 1. Linear voltammogram (three-electrode set-up) of a CdSe cell in the dark. Electrolyte composition: dashed line: 0.5 M KCl, full line: 0.5 M KCl + 0.5 mM $Fe(CN)_6^{3-}$; pH 2.

$$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-} \quad (1)$$

The reaction starts at a potential considerably more positive than the flat-band potential of the semiconductor. This is in accordance with previous observations [14].

The open circles in Fig. 2 ('Electrode 1', Table I) shows the photocurrent-photovoltage curve for this electrode, in hexacyanoferrate(III) solution at pH 6. The fill factor, *FF*, is 0.59, and the photopower at the working point, P_{max}, is 0.49 mW cm^{-2}, giving a conversion efficiency of 0.109. Under the conditions used, the CdSe film photocorroded rapidly, and the photocurrent dropped to zero after less than 1 h of continued illumination (as shown in Fig. 3, open circles).

When the electrode is placed in a hexacyanoferrate(III) solution, also containing In(III) ions, and kept cathodically polarized (-250 mV) for some time, a protective coat was formed on the electrode surface, as evidenced by changes in PEC characteristics (as illustrated in Figs 2 and 3 for one electrode, 'Electrode 5' in Table 1):

(i) The coated electrodes show less favourable *i–V* curves, as shown in Fig. 2 (filled circles). The short-

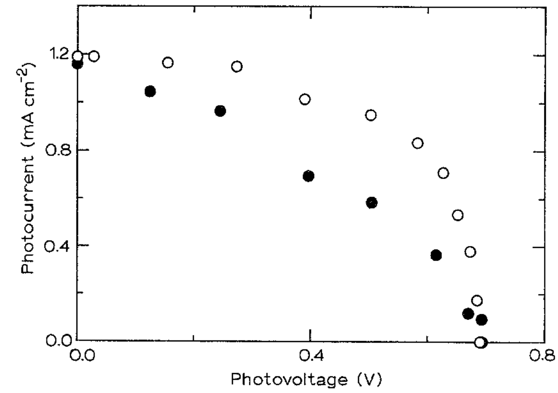

Fig. 2. Photovoltage–photocurrent behavior (two-electrode set-up) for a naked electrode (No. 1, ○) and a coated electrode (No. 5, ●). Electrolyte composition: 0.5 M KCl + 0.5 mM $Fe(CN)_6^{3-}$; pH 6.

Table 1. Parameters of PEC cells modified with indium hexacyanoferrate

Electrode no.	*Charge passed* ($mC\,cm^{-2}$)	I_{sc} ($mA\,cm^{-2}$)	U_{oc} (V)	$I_{sc} \times U_{oc}$ ($mW\,cm^{-2}$)	*FF*	P_{max} ($mW\,cm^{-2}$)	η
1	0	1.19	0.694	0.825	0.59	0.49	0.109
2	7.07	1.17	0.695	0.817	0.56	0.45	0.101
3	14.7	1.16	0.690	0.800	0.36	0.29	0.066
4	15.0	1.14	0.679	0.785	0.39	0.30	0.068
5	35.6	1.16	0.689	0.799	0.39	0.31	0.069
6	34.9	1.13	0.679	0.767	0.39	0.30	0.068
7	56.6	1.08	0.650	0.702	0.32	0.22	0.050

circuit current density and the open circuit voltage are almost the same as for the untreated electrode. The fill factor, however, is appreciably lower, 0.39, and thence P_{max} ($0.310\,mW\,cm^{-2}$) and the conversion efficiency (0.069).

(ii) Photocorrosion is almost entirely suppressed, as shown in Fig. 3 (filled circles). During the first few minutes the photocurrent (measured at the working point of the cell) drops some 5%. From then onwards, however, it remains virtually stable over the time of the experiment, 10 h of continuous illumination.

Prolonged soaking of the electrode in the hexacyanoferrate electrolyte (in the absence of In) at open circuit in the dark results in a decomposition of the coat. Measuring the photocurrent after five days gave a value only one half of the original one. This process is, however, slow compared to what we reported previously for another system [15].

The electrode potential during the coat forming electrolysis is much too positive for reduction of indium(III) ions. The coating formation must then involve hexacyanoferrate(II) ions formed at the cathode surface by Reaction 1. Indium-hexacyanoferrate(II) is known [16] to have low solubility, and a likely candidate for film forming reactions is then

$$4In^{3+} + 3Fe(CN)_6^{4-} \longrightarrow In_4[Fe(CN)_6]_3 \quad (2)$$

However, we cannot rule out an alternative reaction,

$$K^+ + In^{3+} + Fe(CN)_6^{4-} \longrightarrow KIn[Fe(CN)_6] \quad (3)$$

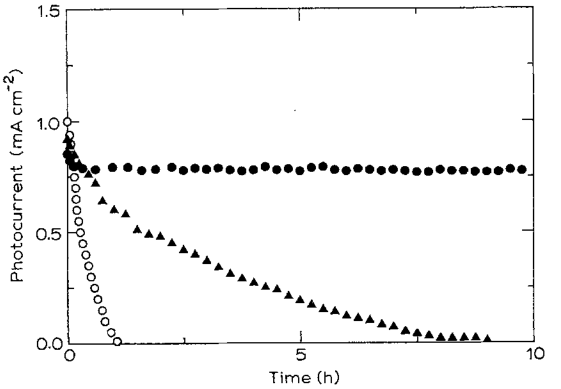

Fig. 3. Long time stability test with continuous illumination, using the two-electrode set-up and measuring the photocurrent at the working point of the cell, both for a naked electrode (No. 1, ○) and two coated electrodes (No. 2, ▲, and No. 5, ●). Electrolyte composition as in Fig. 2.

No attempts were made to ascertain the relative importance of these two possibilities, and we will refer to the coating simply as indium hexacyanoferrate.

Further evidence for the composition the coating comes from ATR FT-IR measurements. As shown in Fig. 4, the ATR FT-IR curve for the modified electrode shows a dip at $2100\,cm^{-1}$, not present for the untreated electrode, and characteristic for Fe(II)–C≡N–In bridges [16].

The coating thickness can be assumed to be proportional to the charge passed during indium hexacyanoferrate deposition. Electrode number 5 in Figs 2 and 3 was passivated by passing a charge of $35.6\,mC\,cm^{-2}$ through the cell. To determine the optimal thickness, this charge was varied from 7 to $57\,mC\,cm^{-2}$, *cf.* Table 1. The efficiency reaches a plateau at $15\,mC\,cm^{-2}$, and starts to fall once more for charges between 35 and $57\,mC\,cm^{-2}$. The highest value, not much lower than for the naked electrode, was observed for an electrode passivated by passing a charge of only $7\,mC\,cm^{-2}$ through the cell. Unfortunately this particular electrode showed inadequate stability, as illustrated in Fig. 3 (triangles).

4. Discussion

When discussing the various observations it must be borne in mind that although every measure was taken to start from CdSe electrodes of identical properties, it cannot be excluded that random variations in some properties of the CdSe film can affect the measured data.

A maximum value for the thickness of the coatings can be obtained on the assumption that all hexacyanoferrate(II) is used for coat formation, and taking an approximate value, $1.8\,g\,cm^{-3}$, for the density of indium hexacyanoferrate. For the two coated electrodes in Fig. 3, No. 2 and No. 5, we obtain the values 0.15 and 0.70 μm, respectively. Already the thinner of these films should provide good protection. Our conclusion is either that the films are much thinner than this calculated maximum, or that they are quite porous. As film growth depends on the concentration of both indium(III) and hexacyanoferrate(II) ions, it is likely that quite some hexacyanoferrate(II) formed is lost by diffusion *to* the bulk of the solution in anticipation of arrival of enough indium(III) by diffusion *from* the bulk.

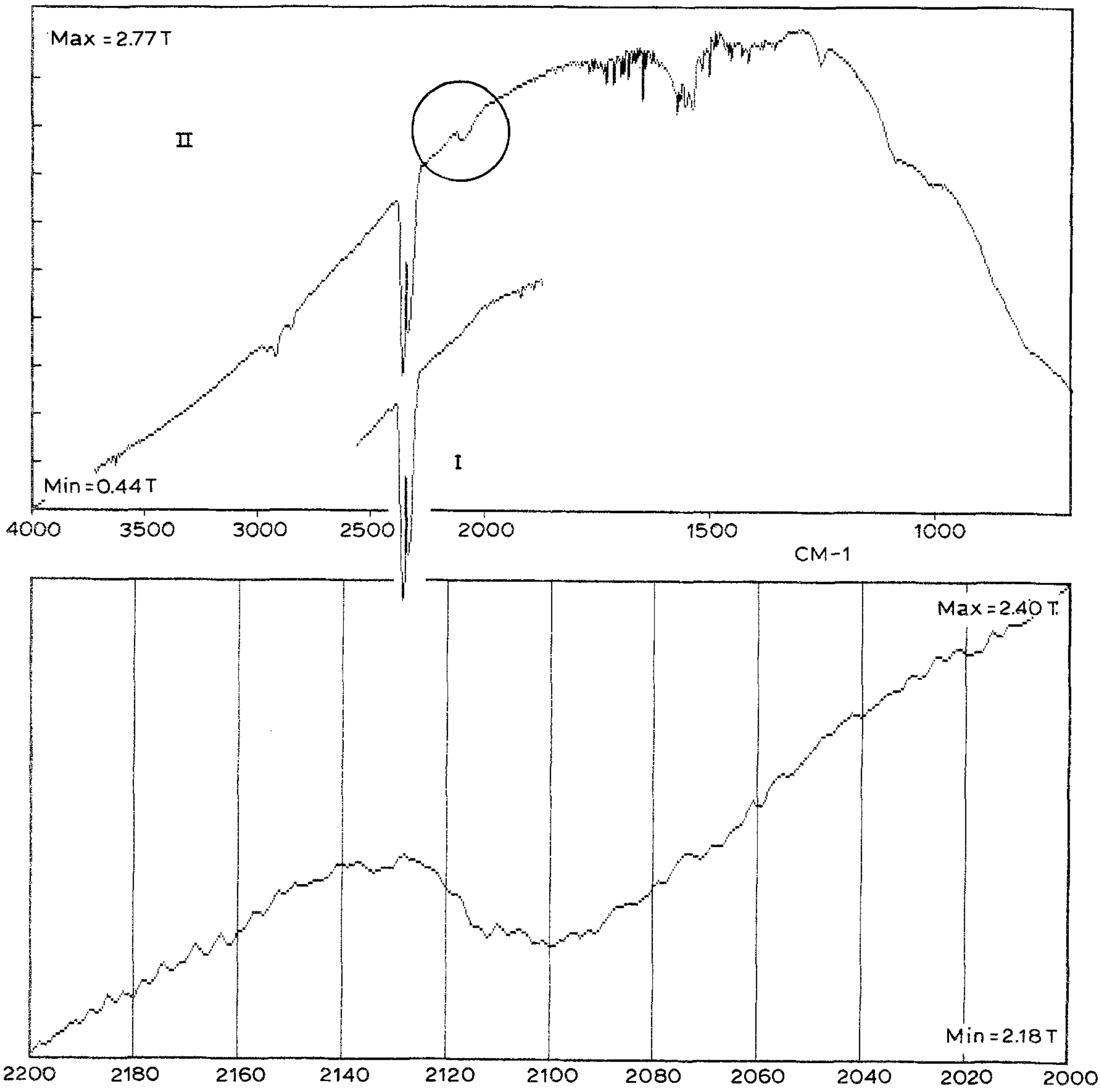

Fig. 4. ATR FT-IR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy) curves: Upper panel: (I) Ti foil + CdSe, (II) Ti foil + CdSe + film. Lower panel: magnification of the encircled part of (II).

The lower values for PEC parameters for coated CdSe electrodes, as compared to naked ones, can have three sources, which would show up in plots like Fig. 2 in different ways:

(i) Light absorption by the coating would decrease both the open circuit voltage, U_{oc}, and the short circuit current density, i_{sc}, without affecting the fill factor, *FF*.

(ii) High resistance in the coating would decrease the photocurrent without affecting U_{oc} or *FF*.

(iii) Surface recombination via new interface states would have little effect on U_{oc} and i_{sc} but lead to a decrease in *FF*.

Data from several experiments are collected in Table 1, and support the following conclusions:

(i) U_{oc} decreases a few percent when going from 0 to 36 mC cm^{-2}, indicating that light absorption by the coating is small but not negligible.

(ii) The relative decrease in U_{oc} and in i_{sc} are very similar, indicating that resistance of the coatings used in our experiments is negligible.

(iii) *FF* drops by a third, indicating that surface recombination is by far the most significant source of efficiency loss. New surface states, acting as recombination centres, are created with the first monolayer of coating. The decrease in *FF* with increasing total charge indicates that, for 'intermediate' coatings, the CdSe surface is incompletely covered with the indium hexacyanoferrate coat. This is consistent with the incomplete protection against photocorrosion exhibited by these electrodes.

Further work will include laterally resolved studies of the material using the fibre optical laser spot technique [17].

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