CdSe Photoanodes for Electrochemical Photovoltaic Conversion

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The paper presents experimental results obtained with a polycrystalline n-CdSe photoanode produced as recently described. The photoelectrochemical studies (I-V and C-V measurements), using a polysulfide electrolyte, indicate a relatively high efficiency of 6.8%.

Key words: Photoelectrochemical solar cells, CdSe, Semiconductor photoelectrochemistry

Introduction

Recently cadmium selenide (CdSe) photoelectrodes attracted interest concerning solar energy conversion because of their good stability and high efficiency. Investigations were performed with CdSe single crystals [1, 2], sintered pellets [3], pastes [4, 5] as well as thin films, obtained by different methods, e.g. electrochemical deposition [6–8], spray pyrolysis [9], vacuum deposition [10] and growth from solutions [11]. The best results with regard to high efficiency (12.4%) are obtained with single n-CdSe crystals in alkaline $K_3Fe(CN)_6/K_4Fe(CN)_6$ electrolyte [1]. However, the semiconductor is not stable, showing surface corrosion. Investigations were also carried out using polysulfide electrolytes. The CdSe photoanodes in this case are stable, even under prolonged operation, showing efficiencies up to 8% [1].

The aim of the present paper was to investigate the photoelectrochemical properties of a recently described n-CdSe photoanode [12] using an aqueous polysulfide electrolyte.

Experimental

Polycrystalline n-CdSe films were prepared by recrystallization on pellets made from CdSe powder (Merck, Suprapur). The powder was pressed at 30 kPa/cm^2 to pellets with up to 1 mm thickness and 8 mm diameter. The recrystallyzation process was performed in the presence of air at 1070–1170 K for 4 hours. During this procedure about 100 μm thin layers of CdSe with a well defined texture and 30–50 μm crystallytes were obtained. Further details will be published elsewhere [12]. All samples were doped by mixing different quantities of $InBr_3$ with the CdSe powder prior to pressing. An ohmic contact was made at the rear of each pellet with an In-Ga alloy, and a copper wire was attached to the electrodes. The back and the sides of the pellets were insulated by means of paraphine.

Various polysulfide aqueous solutions containing Na_2S, S and NaOH were used as electrolyte. The solutions were made from reagent grade chemicals and bidestilled water.

Potentiostatic current-voltage (I-V) curves were measured versus a saturated calomel electrode (SCE) using a platinized Pt counter electrode. Current-voltage characteristics of some samples were tested in a two-electrode scheme as solar cells with brass metal electrodes, coated with Cu_2S according to [13]. Additionally, capacitance-voltage measurements were performed by means of an HP-4274A LCR-meter as described in [14].

A 300 W xenon lamp with water IR filter and with UV-cutoff filter ($\lambda < 300$ nm) was used as light source. The illumination intensity was measured by means of a YSI Kettering (model 65A, Radiometer), taking into account the absorption in the solution.

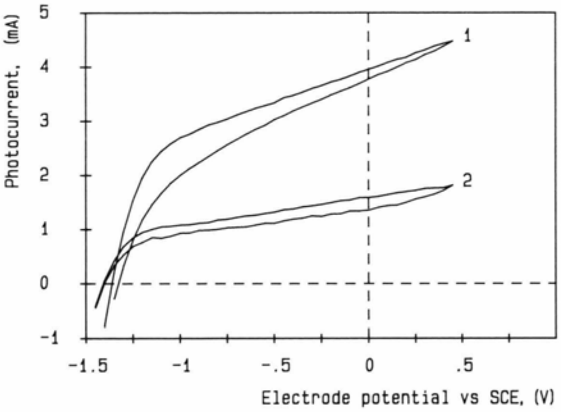

Fig. 1. Potentiostatic current-voltage characteristics of CdSe electrodes. Illumination intensity: 35 mW/cm^2. Electrolyte: 2.5 M Na_2S, 2.5 M S. See text for more details.

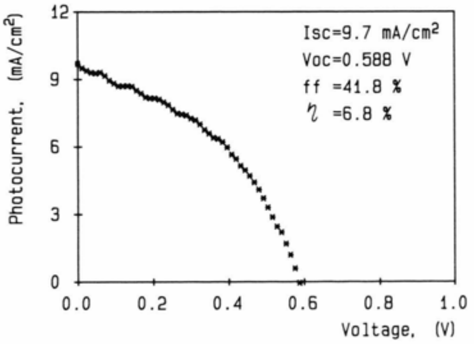

Fig. 2. Current-voltage characteristic of CdSe (doped to 10^{18} cm^{-3}) in 2.5 M Na_2S, 2.5 M S electrolyte with Cu_2S counter electrode. Light intensity: 35 mW/cm^2.

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Results and discussions

Potentiostatic curves measured under illumination for two samples with different In-doping densities are shown in Figure 1. Curve 1 is typical for samples doped in the range of $5 \cdot 10^{17}$–$5 \cdot 10^{18}$ cm^{-3}.

The resistance of these pellets, measured in the dark between the front and the back sides, varied from 1 to 100 Ohm. The donor densities were determined by means of the Mott-Schottky equation using capacitance-voltage data. Samples with a lower doping density (about 10^{15} cm^{-3}) showed dark resistances higher than 10 kOhm. The doping density was approximately derived from the initial concentration of $InBr_3$ in the CdSe powder. A precise determination of the doping density based on the capacitance-voltage data was not satisfactory with the setup being at our disposal [14]. Curve 2, Fig. 1, represents a typical potentiostatic current-voltage dependence resulting under illumination. Surprisingly, the obtained photocurrents were too large for the measured dark resistances. Therefore, the sample resistance was measured under illumination, and a significant decrease of its value (up to 100 Ohm) was observed.

It was further established that the shape of the I-V-curves obtained under illumination, as well as the photocurrent and the onset potential depend essentially on the pretreatment of the electrode. After prolonged illumination at $V = 0.5$ V vs. SCE the photocurrent decreases. In order to obtain its initial value, the electrode was kept for a while at -1.5 V vs. SCE, or the electrolyte was intensively stirred. One may assume that at high current densities sulfur is deposited on the photoanode and the subsequent sulfur dissolution is the rate-limiting step.

For testing the samples as photoelectrodes in a solar energy conversion cell special care was taken to minimize the losses at the counter electrode and in the electrolyte. Hence, electrolytes containing different concentrations of NaOH, Na_2S and S were tested. The best results were obtained with an aqueous solution of 2.5 M Na_2S, 2.5 M S and zero NaOH. The effect of electrolyte composition was studied previously [15, 16].

In the present investigations Cu_2S electroplated on brass plate (5 cm^2) [13] was used as a counter electrode. Current-voltage measurements showed that Cu_2S was much more electrocatalytically active than platinized Pt under otherwise similar conditions.

A current-voltage curve obtained with a CdSe photoelectrode (doped to 10^{18} cm^{-3}) in a solar cell is shown on Figure 2. Short circuit current $I_{sc} = 9.7$ mA/cm^2, open circuit voltage $V_{oc} = 0.588$ V, fill-factor 41.8% under 35 mW/cm^2 light irradiation. The peak conversion efficiency resulting from this measurement is 6.8%.

Although the samples were pellets, their working surface represents a recrystallized thin layer of CdSe with a well defined texture and realtively large crystallytes, which might be responsible for the better photoelectrochemical performance compared with the results previously obtained for sintered pellets [3].

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