Electrodeposition of Thin-film CdSe from Sulphite Solution

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Thin films of CdSe of area 1 cm^2 electrodeposited from sulphite solutions onto Ti plates give light power conversion efficiencies between 5.0 and 5.5%.

The preparation of thin-film CdSe for solar cells by means of electrodeposition from an aqueous solution containing Cd^{2+} and H_2SeO_3 has been studied by a number of workers.[1—4] The mechanism for this deposition process appears complicated because a substantial excess of selenium is detected in the film.[1—3] To remove a major portion of this excess, the films must be annealed at temperatures as high as 750 °C.[3]

It has been suggested that selenium incorporation occurs according to equation (1). Consequently, use of a selenium precursor that is formally in a lower valence state might avoid this undesirable side reaction. For this purpose, we have developed an electrodeposition process that involves the reduction of selenium, which is in the form of the selenosulphite anion $SeSO_3^{2-}$. This species is prepared *in situ* by dissolving finely powdered amorphous black selenium in an aqueous sodium sulphite solution.

$$2CdSe + H_2SeO_3 + 4H^+ \rightarrow 2Cd^{2+} + 3Se + 3H_2O \quad (1)$$

A variety of conditions have been explored and, to date, the films giving the highest light conversion efficiencies (between 5.0 and 5.5%) for 1 cm^2 areas were prepared potentiostatically under the following conditions. A two-electrode cell consisted of a Cd anode and a Ti cathode immersed in an aqueous solution containing 0.30 M Na_2SO_3, 0.04 M Se, 0.024 M nitrilotriacetic acid, and 0.022 M $CdCl_2 \cdot 2.5\ H_2O$ at pH 9 and room temperature. A potential of 0.23 V was applied for 1 h, during which a nearly constant current of 0.25 mA was maintained. The dark grey smooth film on Ti was annealed at 500 °C in air for 1 h with no visible change in appearance. After etching the film in 9 M HCl for 20 s and soaking it in 2 M NaOH, the deposition process was repeated for one additional hour. Based on the density of CdSe and the weight of the films, the thickness is estimated to be between 2.3 and 2.6 µm. Annealing at 550 °C for 30 min in air to improve its photoresponse (500 °C anneal gives efficiencies between 3.5 and 4.0%) caused a slight darkening of the film. The films were treated with 9 M HCl and 1 M $ZnCl_2$[5] prior to power measurements.

In the selenosulphite solution Cd^{2+} is known to react chemically to form CdSe.[6—8] Nitrilotriacetic acid is employed to complex Cd^{2+} (stability constant, $10^{9.5}$),[9] thereby reducing the concentration of free Cd^{2+} to the point that the rate of precipitation of CdSe *via* this, the unwanted, chemical reaction is slowed substantially. Control experiments indicate that no film is observed unless the potential is applied. At higher selenosulphite concentrations, a slight excess of selenium is incorporated into the film. Also, higher current densities (*ca.* 2 mA/cm^2) appear to cause incorporation of metallic Cd.†

The photocurrent–photovoltage characteristics of the CdSe films were measured using a two-electrode cell consisting of a Cu_2S-on-brass screen counter electrode, a solution of Na_2S–S–NaOH (each 1 M),[10] and a variable resistance load provided by a decade resistance box. The CdSe electrodes, which had areas *ca.* 1 cm^2, were illuminated with 70 mW unfiltered light from a 300 W CGE Quartzline ELH lamp. No biasing was applied to the semiconductor electrode. No corrections were made for reflection and absorption losses.

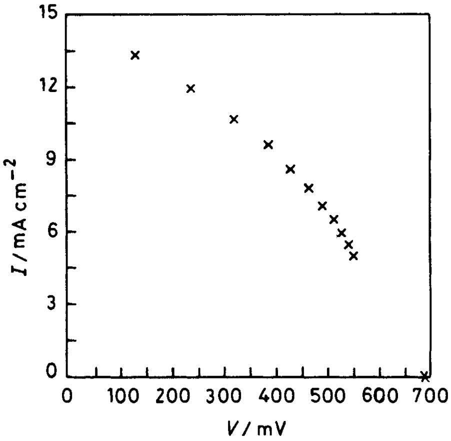

Figure 1. Current–voltage characteristics of electrodeposited thin-film n-CdSe (area 1.0 cm^2) in aqueous Na_2S–S–NaOH (each 1 M). Measurements were made using a cell that consisted of two electrodes connected with a variable resistance load. $V_{o.c.}$ = 0.685 V is the maximum value observed (see text). Dark currents were negligible at all loads. Power input from ELH lamp: 70 mW/cm^2; maximum power output from cell: 3.66 mW/cm^2.

Figure 1 illustrates the photocurrent–photovoltage behaviour of a typical CdSe film. This particular film, which had a surface area of 1.0 cm^2, gave a power conversion efficiency of 5.2%. Dark currents were too small to measure at all loads, providing another indication of the quality of the film. A number of films grown using the conditions presented above gave power conversion efficiences between 5.0 and 5.5%. For comparison, carefully optimised cells incorporating CdSe films grown from H_2SeO_3–Cd^{2+} had 6.4 and 6.7% power conversion efficiencies using 100 and 80 mW, respectively, of artificial light from an ELH lamp.[3,4] However it should be noted that either the surface area of this film was substantially smaller than 1 cm^2 (namely, 0.22 cm^2)[3] or adhesion was a problem.[4] Thin-film CdSe has also been electrodeposited from CN^- solutions in which elemental selenium has been dissolved. However, the reported efficiencies are low.[11]

During illumination, the voltage (current) readings were constant over the period of the measurement (*ca.* 15 min) at all loads except at open circuit (o.c.). For the latter, $V_{o.c.}$ started at 587 mV, increased to 685 mV during 15 min, and then slowly decreased to 574 mV and remained steady. Maximum $V_{o.c.}$ is included in Figure 1, although the fill factor ($P_{max.}/I_{s.c.}V_{o.c}$) would be increased if the minimum $V_{o.c.}$ were employed.

Studies aimed at improving the output of CdSe films of 1 cm^2 or larger area will be presented later. These studies will include detailed surface analysis using Rutherford backscattering (R.B.S.) spectroscopy with 1.6 MeV α particles. Preliminary results indicate that the Cd/Se ratio is 1.0 ± 0.1 for CdSe films grown on Ti.

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† The details of the surface analysis will be presented elsewhere.

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