ELECTROCHEMICAL METHOD FOR IMPROVING THE SPECTRAL RESPONSE OF CdS/Cu$_2$S HETEROJUNCTIONS

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Summary

The effect on the stoichiometry of a copper sulphide electrode of short-circuiting the Cu/Cu$_{aq}^{2+}$/Cu$_{2-\delta}$S/In galvanic cell for different times has been studied. This treatment has been carried out on the copper sulphide layer of CdS/Cu$_2$S solar cells prepared by different methods. The resulting changes of the spectral short circuit current and the *I–V* characteristics of the cells have been recorded. Remarkable increases in open circuit voltage, short circuit current, and fill factor have been observed as a consequence of any transformation that increases the proportion of copper in the copper sulphide films. Thus, this treatment could be a suitable method of improving the efficiency of CdS/Cu$_2$S solar cells.

1. Introduction

It is generally accepted that a strong correlation exists between the efficiency of CdS/Cu$_2$S solar cells and the composition and structure of their copper sulphide layer. Chalcocite has been identified as the phase producing the most efficient cells [1], and the degradation of these cells has been associated with the transformation of the chalcocite layer into less stoichiometric cuprous sulphides (such as djurlite) by different mechanisms [2]. Simple oxidation (generally due to atmospheric oxygen) and electrochemical decomposition caused by the electrical field formed at the heterojunction are some of the processes involved [3]. These processes can be reversed by subjecting the non-stoichiometric copper sulphide layer to a reduction process that brings the layer composition nearer to stoichiometric cuprous sulphide.

In this work we have deliberately modified the non-stoichiometric cuprous sulphide layers of CdS/Cu$_2$S solar cells, fabricated by different methods, by short-circuiting the galvanic cell Cu/Cu$_{aq}^{2+}$/Cu$_{2-\delta}$S/In where the

$Cu_{2-\delta}S$ term is the copper sulphide film belonging to a solar cell. The overall reaction at the galvanic cell studied is:

$$Cu_{2-\delta_1}S + (\delta_1 - \delta_2)Cu \longrightarrow Cu_{2-\delta_2}S \tag{1}$$

where δ represents the deviation from stoichiometry. From the equilibrium conditions at interfaces it follows [4] that:

$$\mu_{Cu}^0 - \mu_{Cu}^{Cu_xS} = 2FE \tag{2}$$

E being the e.m.f. of the cell. Thus, following Rickert, we can take the cell e.m.f. as a measure of the chemical potential of copper in the copper sulphide. Equation (2) shows that if the galvanic cell is short-circuited, the cell reaction, eqn. (1), proceeds in the forward sense, the Cu_xS being converted into a phase richer in copper. If the short-circuiting time was sufficiently long, the cell e.m.f. became zero, which means that all the copper sulphide layer has been transformed into Cu_2S.

This method has been used to study the influence of Cu_xS stoichiometry on the photovoltaic properties of CdS/Cu_2S solar cells fabricated by two methods; i.e., by the Clevite method and by the Phillip's solid state ion-exchange method.

We observed how the efficiencies of these cells are improved when their copper sulphide layers are transformed into phases richer in copper by successive treatments. The results obtained suggest that these treatments can be used to improve the efficiencies of CdS/Cu_2S solar cells.

2. Experimental

The solar cells studied have been obtained by topotaxial growth of Cu_xS on CdS evaporated films, following two conventional methods:

(a) The Clevite method [5]. Thin CdS films are etched with a 1:1 solution of HCl in H_2O for 12 s. The Cu_2S layer is produced by dipping in acid solution (pH = 3.5) with a concentration of 6 g/l of CuCl and 2 g/l of NaCl. The temperature of the solution is 95 °C and the dipping time is about 8 s.

(b) The dry method [6]. Samples were prepared by evaporation of 1500 Å of CuCl on CdS which was kept at 40 °C. A vacuum treatment at 200 °C for 5 min is given to complete the ionic exchange reaction. After this, the sample was removed, washed with distilled water and dried in air to avoid residual $CdCl_2$.

We changed the initial stoichiometry of the copper sulphide layer in these cells by short-circuiting the galvanic cell, eqn. (1), for various times.

The stoichiometry of the films was determined using the method proposed by Castel and Vedel [7] based on the measurement of the e.m.f. of the cell

$$Cu/Cu_{aq}^{2+}/Cu_xS/In$$
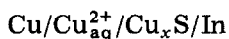
The working conditions involving the reference system, noise control, and stability have been described previously [8].

Spectral short circuit current measurements were made on the solar cells in the "as grown" conditions and after successive short-circuit treatments for various times. A grating monochromator with a tungsten lamp was used in these measurements.

The $I-V$ characteristics of the cells were recorded at each step of the experiment. Cell measurements were made by pressing a gold-plated grid over the copper sulphide layer using suction and illuminating in the "front wall" mode. Electrical contact was not as good as that provided by the conventional evaporated or laminated grids and therefore the measured short circuit currents are not maximum values but are to be taken as indicative. However, this method allows successive treatments to be carried out on a single sample and their effect on the photovoltaic properties of that sample to be followed.

3. Results and discussion

Two CdS/Cu$_x$S solar cells prepared by the Clevite method were subjected to the short-circuiting treatment described in the preceding section. The copper sulphide films of the as-grown cells had the stoichiom-etries $x = 1.940$ for cell C.1 and a value lying between $x = 1.960$ and $x = 1.995$ for cell C.2. Djurlite, and a mixture of djurlite and chalcocite are the phases present in these cells, respectively, according to our e.m.f. measurements. This is confirmed by the shape of the spectral responses of the cells (Figs. 1 and 2). In fact, it is observed that the spectral response of the as-grown cell, C.1 (Fig. 1, curve (a)), presents only one peak at 715 nm. This peak has been shown to be representative of pure djurlite, while a 920 nm peak is associated with chalcocite [9, 10]. The coexistence of both peaks, as in the spectral response of the as grown cell C.2 (Fig. 2, curve (a)), indicates that the film consists of a mixture of chalcocite and djurlite.

A 30 minute room temperature short-circuit treatment was given to cell C.1. Cell C.2 was subjected to a similar 20 min treatment. The e.m.f. measurements for the final stoichiometries of the copper sulphide films of these cells give the values $x = 1.995$ and $x = 1.997$, respectively, which correspond to chalcocite phase compositions. The corresponding spectral responses (Figs. 1 and 2, curves (b)) indicate, by contrast, that together with the chalcocite phase, indicated by the 920 nm peaks, some residual djurlite remains in the films since the 715 nm peaks are still present. As the spectral response of a solar cell mainly depends on the structure of the layers next to the junction, while our electrochemical measurements mainly give information about the stoichiometry of the outer layers, these results suggest that the short-circuit treatment first affects the surface layers, which are soon transformed into chalcocite. Then its action is extended to the deeper layers, which are transformed more slowly. In any case, the spectral response increases for all
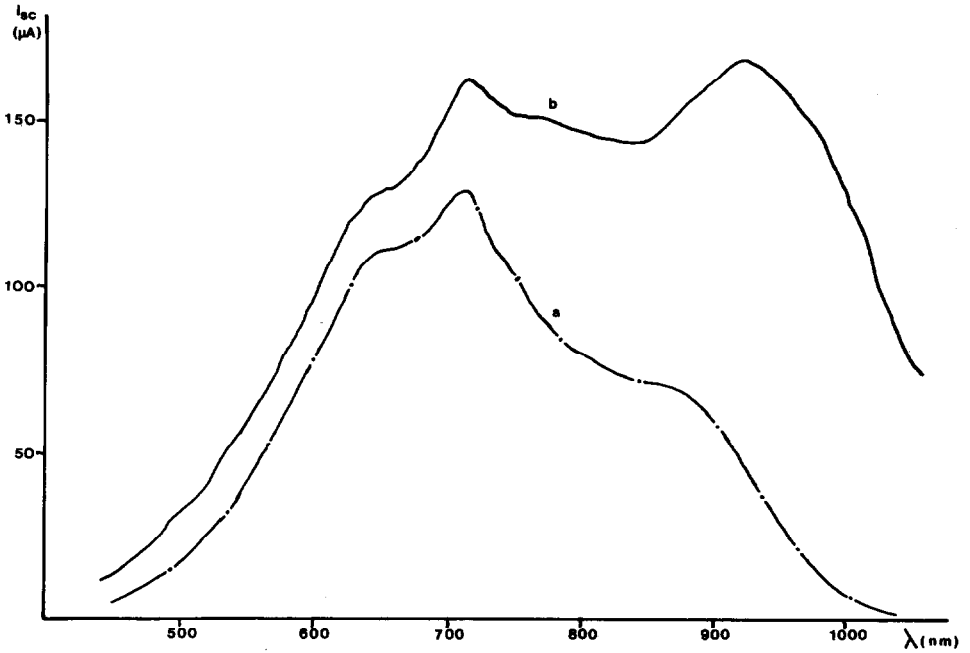
Fig. 1. Spectral short circuit currents of a CdS/Cu$_x$S solar cell (cell C.1) prepared by the Clevite method. (a) As-grown cell; (b) the same cell after a 30 min treatment.
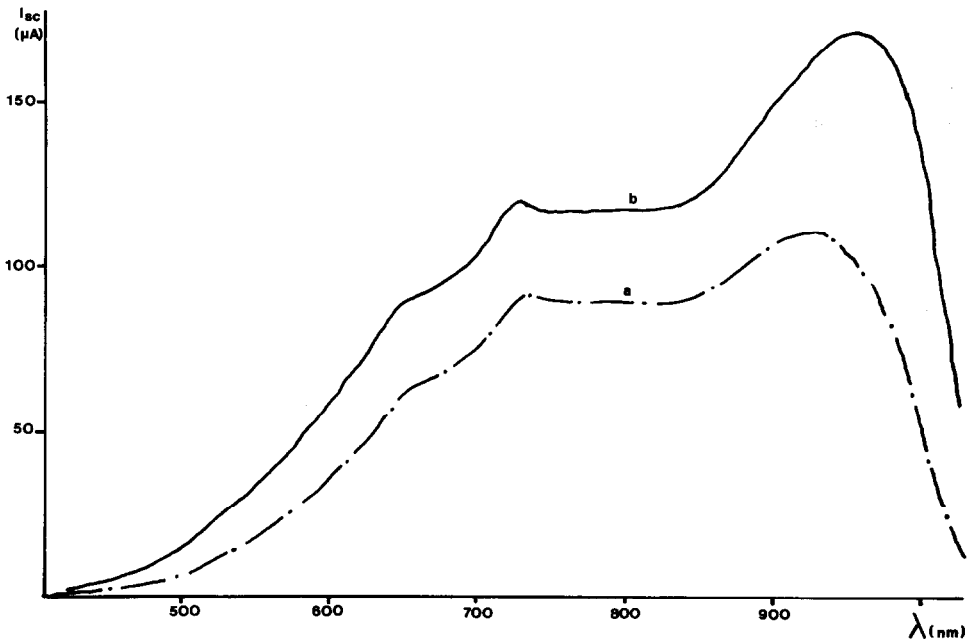

Fig. 2. Spectral short circuit currents of a CdS/Cu$_x$S solar cell (cell C.2) prepared by the Clevite method. (a) As-grown cell; (b) the same cell after a 20 min treatment.

wavelengths as a result of the treatment and, consequently, higher values of the short circuit current of the cells are to be expected.

Figures 3 and 4 show the variations with treatment of the $I-V$ characteristics of cells C.1 and C.2, respectively. Remarkable increases in short circuit current and open circuit voltage are observed in both cases. Smaller variations in the fill factor are also observed. In consequence, important increases in the efficiency of the cells are obtained.
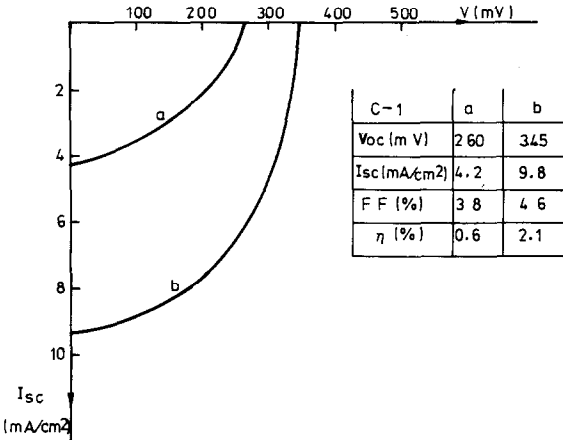
C−1	a	b
Voc (m V)	2 60	345
Isc (mA/cm2)	4. 2	9.8
F F (%)	3 8	4 6
η (%)	0.6	2.1

Fig. 3. $I-V$ characteristics of cell C.1. (a) As-grown cell; (b) the same cell after a 30 min treatment. Illumination: 100 mW cm^{-2}.

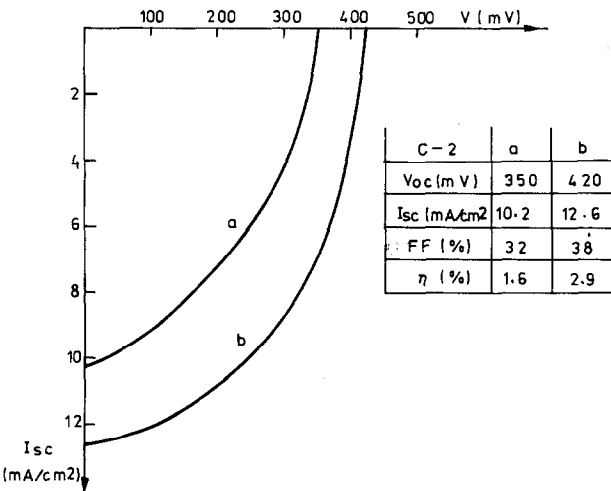| C−2	a	b
Voc (m V)	350	4 20
Isc (mA/cm2)	10·2	12·6
F F (%)	3 2	3 8
η (%)	1·6	2.9

Fig. 4. $I-V$ characteristics of cell C.2. (a) As-grown cell; (b) the same cell after a 20 min treatment. Illumination: 100 mW cm^{-2}.

A third cell (T.11) was prepared by the solid-state ion exchange method. The stoichiometry of the copper sulphide film in the as-grown cell was $x = 1.770$, which corresponds to the digenite phase. Two successive 20 minute treatments were then given to the cell. The stoichiometry of its copper
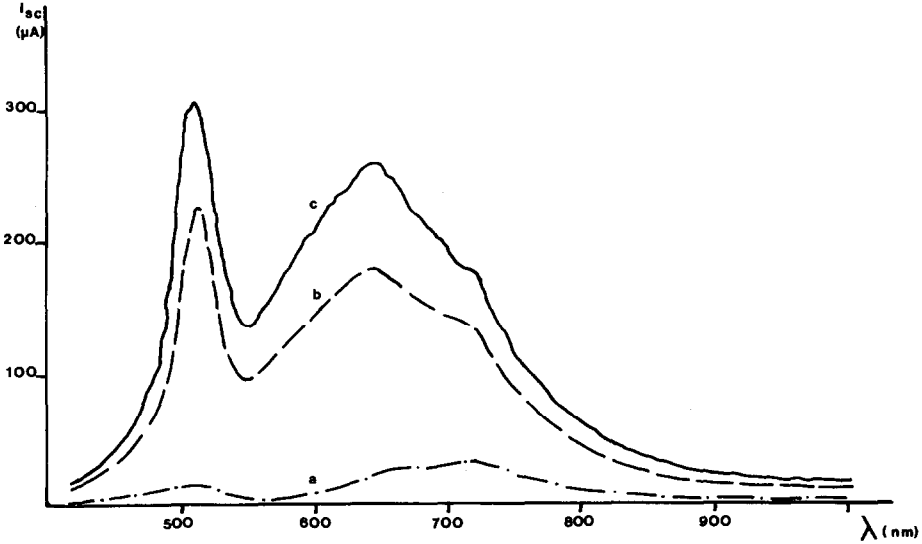

Fig. 5. Spectral short circuit current of a CdS/Cu$_x$S solar cell (cell T.11) prepared by the Phillip's solid-state ion interchange method. (a) As-grown cell; (b) the same cell after a 20 min treatment; (c) the same cell after a 40 min treatment.
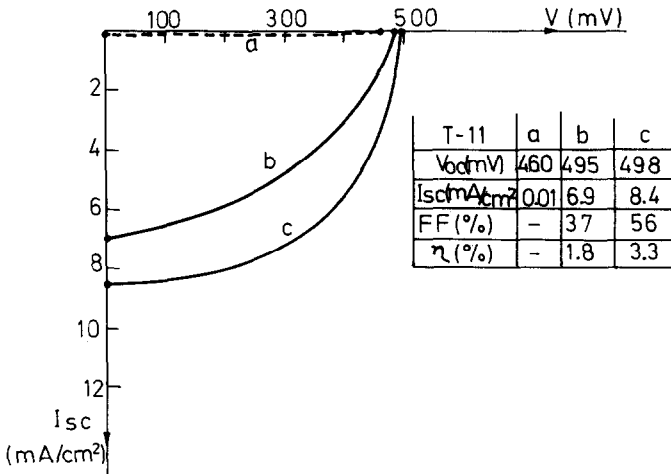

T-11	a	b	c
Voc(mV)	460	495	498
Isc(mA/cm²)	0.01	6.9	8.4
FF(%)	–	37	56
η(%)	–	1.8	3.3

Fig. 6. I–V characteristics of cell T.11. (a) As-grown cell; (b) after a 20 min treatment; (c) after a 40 min treatment. Illumination: 100 mW cm⁻².

sulphide film reached values of $x = 1.950$ and $x = 1.955$ after each of these treatments. Further efforts to transform the copper sulphide layers into chalcocite were fruitless. Figure 5 shows the variation of the spectral response of the cell with these treatments. It will be observed that the major variation occurs with the first treatment, which produces the transformation digenite/djurlite. In consequence of this transformation, the short circuit current increases from 0.01 mA/cm^2 to 6.9 mA/cm^2, while the open circuit voltage only experiences a minor variation from 460 mV to 495 mV and the fill factor increases from 37% to the final value of 56%. Further increases in the cell parameters occur as a result of the second treatment, as may be observed in Fig. 6.

4. Conclusions

The transformation of the copper sulphide film of CdS/Cu$_x$S solar cells into phases nearer to the stoichiometric cuprous sulphide has been carried out by short-circuiting the galvanic cell that this layer forms with a copper electrode in 0.1M copper sulphate solution. The transformation from digenite to djurlite and from this to chalcocite is accomplished in a treatment time of less than 60 min. By combining e.m.f. measurements of the stoichiometry, and solar cell spectral response analysis, a good insight into the evolution of the copper sulphide transformations is obtained. The treatment first affects the surface layers, which are soon transformed into richer copper phases, and then the deeper layers which are transformed more slowly. The transformation is particularly straight forward when it is undertaken on cells produced by the Clevite method. Short circuit current is the solar cell parameter that undergoes the largest increase with the treatment, but open circuit voltages and fill factor also undergo important increases. In consequence, very remarkable improvements in the efficiency of CdS/Cu$_2$S solar cells are obtained by this simple electrochemical treatment.

Acknowledgement

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