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EFFECT OF GREEN LIGHT ON SPECTRAL RESPONSE OF CUPROUS SULFIDE - CADMIUM SULFIDE PHOTOVOLTAIC CELLS

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SUMMARY

Cadmium sulfide (CdS) solar cells consist of an evaporated layer of n-type CdS covered with a thin film of p-type cuprous sulfide (Cu_2S). The response of these cells to red light increases on exposure to green light. The absolute quantum yield of a single-crystal CdS cell was measured under various conditions to aid in understanding this effect. Before heat treatment, the quantum yield was not affected at all by green light. After heat treatment, the quantum yield in the red part of the response spectrum was greatly reduced, but green light restored it to nearly its value before the heat treatment. In another experiment, the current-voltage characteristic of a CdS film cell was measured under red and white light. Analysis of the characteristic curves showed the series resistance of the cell in red light to be 2 orders of magnitude larger than that in white light. These results were interpreted as follows: Heat treatment causes copper to diffuse into the CdS, which produces a layer of copper-compensated CdS having a high dark resistance. This layer is highly photoconductive. Its resistance is greatly lowered by green light but only slightly by red light. Consequently, under red light, the current from the cell is limited by a high series resistance. Under green light, this limit is removed, and the sensitivity of the cell to red light is increased.

INTRODUCTION

Cadmium sulfide (CdS) film solar cells consist of an evaporated layer of n-type CdS covered with a thin film of p-type copper sulfide (Cu_2S), principally chalcocite (refs. 1

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and 2). The spectral response of these cells can be divided into two regions: an extrinsic response to photons with energies less than the CdS band gap of 2.4 electron volts (3.84×10^{-19} J), and the intrinsic response to photons with energies greater than 2.4 electron volts (3.84×10^{-19} J). Secondary illumination changes the spectral response of the cells. This change is shown by illuminating with a constant intensity, constant wavelength light, while the spectral response is measured in the usual way by illuminating the cell with light of various wavelengths. If the secondary light is green or blue (photon energies greater than the CdS band gap), the extrinsic (red and near-infrared) response of the cell is increased, but generally the intrinsic (blue and green) response is unaffected. This response is illustrated in figure 1 (from ref. 2), where the spectral response of a CdS film photovoltaic cell is shown with and without green secondary illumination. This effect has been under study by Shiozawa and his coworkers (ref. 3). They have suggested that photoconductivity in an i-layer in the CdS film is responsible.

A similar spectral response and a similar effect of green light has been observed for a copper - cadmium sulfide (Cu - CdS) photovoltaic cell (ref. 4). The origin of the extrinsic response of the cell was not explained, but the effect of green light was attributed to the depopulation of impurity levels in the forbidden gap of CdS. The increased photocurrent in the presence of green light was assumed to result from the creation of minority carriers in the CdS by transitions of electrons from the valence band to the impurity levels. The impurity levels were assumed to be emptied by the green light, which made possible infrared absorption causing the transition of electrons from the valence-band edge to the impurity states.

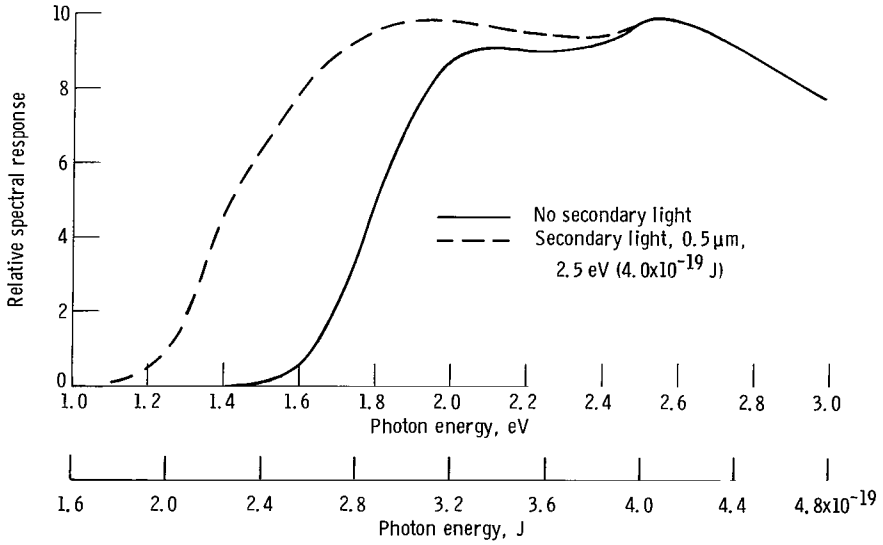


Figure 1. - Effect of green light on spectral response of cuprous sulfide - cadmium sulfide film photovoltaic cell (ref. 2).

The spectral response of Cu_2S - CdS cells, prepared from single-crystal CdS, was measured before and after heat treatment, and with and without green secondary illumination. The junction characteristic of a heat-treated CdS film cell was measured in red and white light. The fact that some experiments were done with crystal cells and some with film cells is not significant, since both have the same spectral response characteristics. Commercial film cells were preferred for the junction-characteristic measurements because of the high quality junctions found in these cells. From the experimental results on crystal and film cells, an explanation was devised for the effect of green light on the spectral response.

EXPERIMENTAL PROCEDURE

Preparation of the Cells

The single-crystal cell was prepared in a way similar to that of the commercial thin-film solar cell (ref. 1). A 10- by 10- by 1-millimeter single-crystal of 5-ohm-centimeter indium-doped CdS was given a light etch in a 10-percent solution of hydrochloric acid; then one side was dipped in a saturated solution of cuprous chloride at 90° C for 5 seconds. A semitransparent (1000- to 2000-Å-thick or 0.1 to 0.2 μm-) film of p-type Cu_2S on the surface of the crystal was produced by the resulting chemical reaction. Electrical contact to the CdS was made with indium solder, while contact to the Cu_2S film was made by an 80-line-per-inch, 85-percent-light-transmission gold grid. The grid was placed on a transparent plastic plate into the surface of which channels were cut. These channels were connected to a vacuum line so that when the crystal was placed on the plate and the vacuum applied, atmospheric pressure forced the crystal into firm contact with the gold grid. Measurements of cell performance were made both before and after the heat treatment of 15 minutes at 240° C in air.

The film cells used in this research were prepared by the same process as was the crystal cell just described. Vacuum evaporated films of CdS on plastic substrates coated with conducting silver paint were used. Contact to the Cu_2S surface layer was made by a gold grid laminated in plastic.

Measurement of Quantum Yield

The quantum yield of the photovoltaic cell was defined as the number of electrons yielded per photon absorbed within a minority-carrier diffusion length of the junction. This quantum yield is equivalent to the collection efficiency of the junction if it is as-

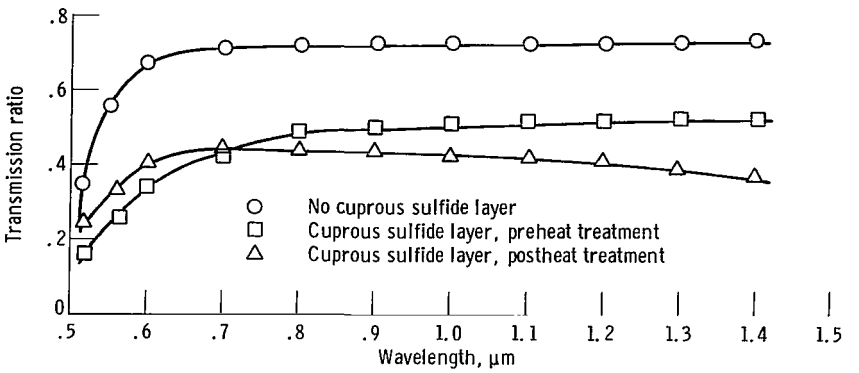


Figure 2. - Transmission of cadmium sulfide crystal with and without cuprous sulfide layer.

sumed that each absorbed photon produces one minority carrier. The diffusion length in Cu_2S is unknown. However, the Cu_2S film was estimated to be only 1000 to 2000 Å (0.1 to 0.2 μm) thick (from chemical analyses of films on similar crystals) so that it was assumed that all the light absorbed by the Cu_2S was within a diffusion length of the junction. The minority-carrier diffusion length in CdS is certainly less than 10 microns, and the crystal thickness was 1 millimeter. Consequently, by illuminating the junction through the CdS, no more than 1 percent of the light that is absorbed by the crystal is absorbed within a diffusion length of the junction. Transmission measurements of the crystal are shown in figure 2. The transmission ratio, which is the ratio of transmitted to incident light intensity, is plotted against wavelength in this figure. If we confine ourselves to the extrinsic region, the transmission of the crystal is approximately constant, near 70 percent. The average reflectivity of the crystal in this spectral range was 23 percent, so that the crystal only absorbs about 7 percent of the incident radiation. Since only a hundredth of this radiation is effective in producing a photocurrent (based on the diffusion length condition), the light absorbed by the CdS in computing the quantum yield can be neglected. From these considerations, the photons absorbed within one diffusion length of the junction were taken to be the incident photon flux multiplied by the difference in transmission of the crystal before and after application of the Cu_2S film. Figure 2 shows the transmission curves used for the calculation. Because the crystal was illuminated from the CdS side, quantum yields were calculated only for the extrinsic response, since green light was absorbed at the CdS surface, far from the junction, and yielded no photocurrent.

The secondary illumination was 0.5-micron blue-green light, referred to hereinafter as green light, with an intensity of approximately 0.1 milliwatt per square centimeter. The green light was furnished by a tungsten lamp masked by an interference

filter having a peak transmission at 0.5-micron and a 20-Å (2×10^{-3}-μm) half-power band pass. For this light to reach the junction region, the Cu_2S side of the cell was illuminated. The intensity of the secondary illumination was high enough to saturate the increased extrinsic response.

DISCUSSION

Quantum Yield

The quantum yield of the cell before and after heat treatment, and with and without green secondary light, is shown in figure 3. Before the heat treatment, no effect of secondary light was noted. After heat treatment, the response in the absence of secondary light was smaller by nearly an order of magnitude. The application of green secondary

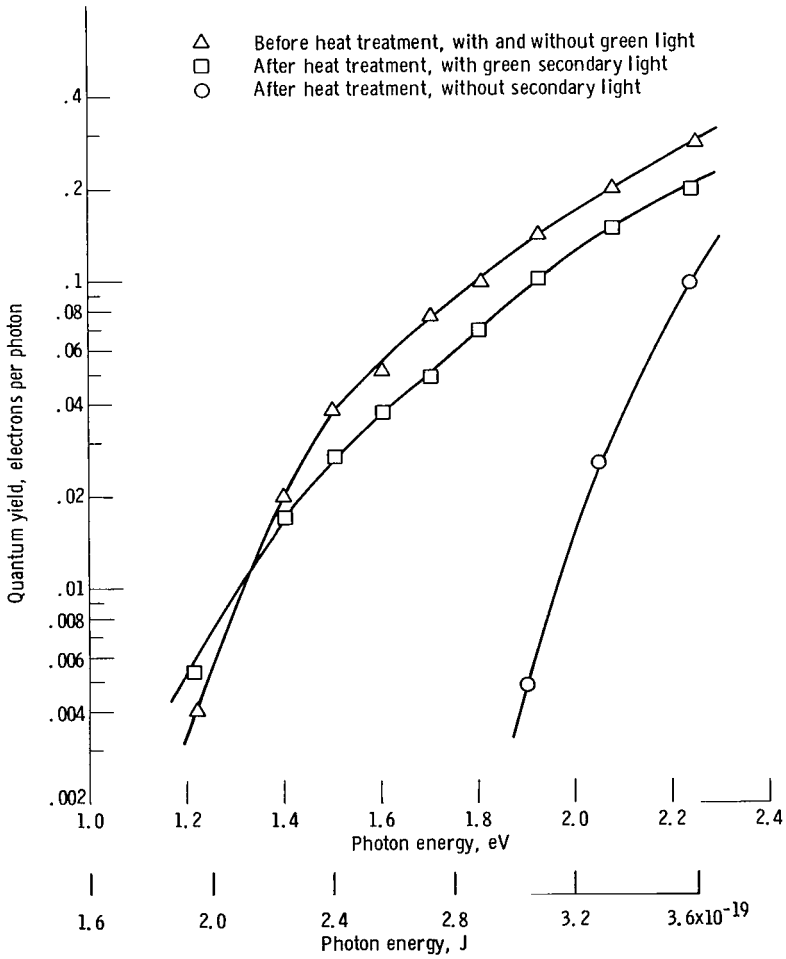


Figure 3. - Quantum yield of cuprous sulfide - cadmium sulfide photovoltaic cell.

light restored the yield to within about 40 percent of its value prior to the heat treatment.

Although the heat treatment lowers the quantum yield, it is a necessary step in solar cell fabrication. Before this step, the open-circuit voltage is low, and the current-voltage characteristic is almost linear. Great improvements in both the open-circuit voltage and the current-voltage characteristic are produced by the heat treatment.

It is significant that the extrinsic response of the cell existed before any heat treatment. In the preparation of the cell, it is dipped into a hot aqueous solution of copper chloride at 90° C for 5 seconds. It seems unlikely that exposure to this low temperature for such a short time could produce much diffusion of impurities into the CdS. Consequently, nearly all the light must be absorbed in the Cu_2S. It follows that the so-called extrinsic response of the cell actually results from minority-carrier generation in the Cu_2S layer.

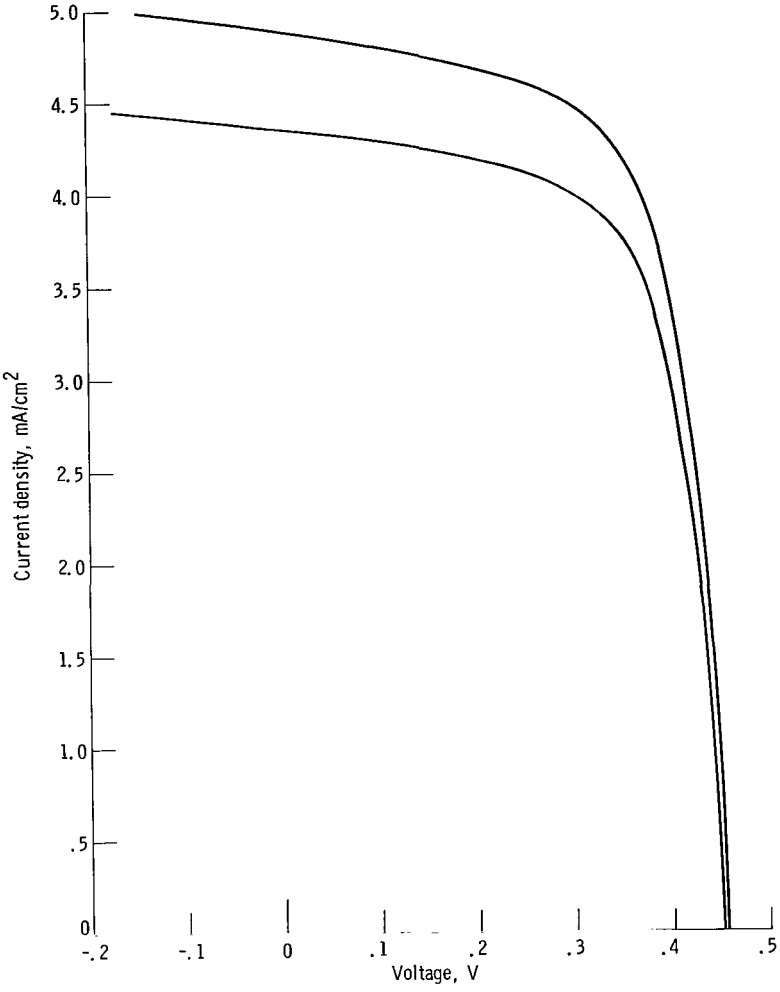
Heat treatment considerably reduces the quantum yield, which implies that diffusion of impurities into the Cu_2S and/or CdS has occurred and that the effect of these impurities is to lower the collection efficiency of the junction. However, heat treatment is necessary to produce enhancement of the extrinsic response by secondary green light, which indicates that the enhancement effect results from impurities introduced into either the CdS or Cu_2S layers by diffusion. The effect of the green secondary light is to return the quantum yield to near its value before heat treatment and implies that the effect of the green light is to nullify partly the electrical effect of the diffused impurity.

To produce the enhancement, the secondary light must have photons with energies greater than that of the CdS band gap; thus, hole generation in the CdS is required.

Current-Voltage Characteristics of Heat-Treated Cell in Red and White Light

The effect of green light on the junction can be understood more clearly if the current-voltage characteristic of a cell is measured in red light (0.8 to 1.2 μm) and in white (3200° K tungsten) light. For this experiment a 2-square-centimeter, 4-percent efficient, heat-treated CdS film cell was used. For each kind of illumination, two slightly different light intensities were used, which yield two current-voltage curves. Two different intensities allow the calculation of the series resistance of the cell by the method of Wolf and Rauschenbach (ref. 5). The resulting curves are shown in figure 4. The intensities of the red and white lights were adjusted to give approximately similar short-circuit current values.

Since white light contains both red and green light, the electrical nature of the junction under white light illumination is expected to be similar to that existing when spectral response is measured in the red part of the spectrum in the presence of green secondary



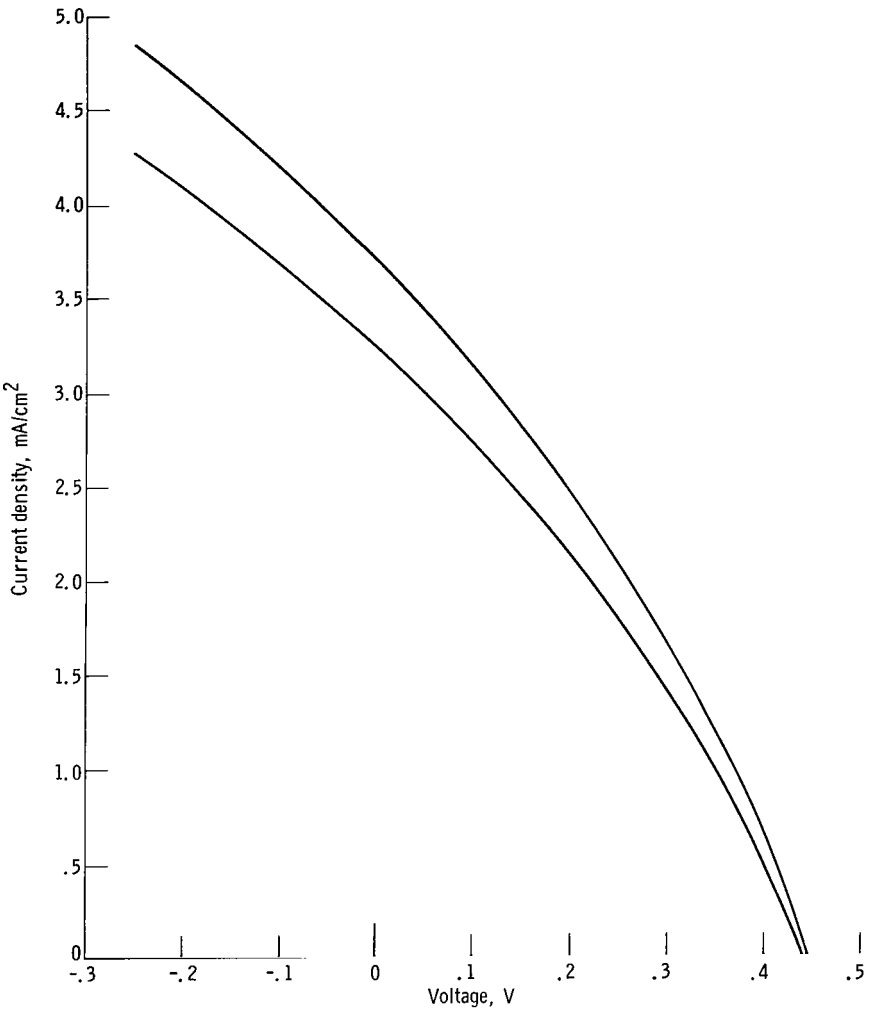
(a) White light.

Figure 4. - Current-voltage curves for cadmium sulfide film cell at two light intensities.

light. The red and white light produce quite different current-voltage curves, which indicate a difference in the electrical nature of the junction under these two illumination conditions. The equation that describes the current-voltage characteristic of a solar cell is (ref. 5)

$$I = I_o \left\{ \exp\left[\frac{e(V - IR_s)}{AkT}\right] - 1 \right\} + I_L + \frac{V - IR_s}{R_{sh}} \tag{1}$$

The equation given in reference 5 was made more general by the inclusion of the shunt resistance R_{sh}. The other symbols are defined as follows: I, the current from the cell;



(b) Red light.

Figure 4. - Concluded.

I_o, the reverse saturation current; e, the charge on the electron; V, the voltage appearing at the terminals of the cell; R_s, the series resistance; A, a dimensionless constant equal to 1 for an ideal junction; k, Boltzmann constant; T, temperature, and I_L, the light-generated current. The equation contains four constants that describe the junction: I_o, R_s, R_{sh}, and A. The method of Wolf and Rauschenbach (ref. 5) was used to find the series resistance from the two current-voltage curves. In this method, the voltages corresponding to a given current increment are measured for the two curves. The difference between the two voltages divided by the current increment is the series resistance. Wolf and Rauschenbach (ref. 5) noted that the series resistance calculated by this method varied with the size of the current increment chosen. In the present work, a current

increment equal to the short-circuit current of the lower current-voltage curve was chosen. This increment yielded an average series resistance for the whole current-voltage curve.

Many methods of finding the remaining constants are possible. A method which included as much as possible of the current-voltage curve was used, and the following procedure was adopted: If the true cell voltage is defined as V', equal to $V - IR_s$, and if this variable is substituted into equation (1) and differentiated, the resulting equation is

$$\frac{dI}{dV'} = \frac{I_o e}{AkT} \exp \frac{eV'}{AkT} + \frac{1}{R_{sh}} \tag{2}$$

At the true short-circuit condition, where $V' = V - IR_s = 0$,

$$\frac{dI}{dV'} = \frac{I_o e}{AkT} + \frac{1}{R_{sh}} \tag{3}$$

At the open-circuit condition,

$$\frac{dI}{dV'} = \frac{I_o e}{AkT} \exp \frac{eV_{oc}}{AkT} + \frac{1}{R_{sh}} \tag{4}$$

where V_{oc} is the open-circuit voltage.

These equations show that the effect of shunt resistance on the current-voltage characteristic cannot be easily distinguished from the effect of the reverse saturation current. The physical significance of the shunt resistance is a metal-like conduction path through the junction region. In a well-made cell, there should be few of these paths. The analysis can be simplified by assuming that the shunt resistance terms in equations (3) and (4) are negligibly small in a high-efficiency cell (3 to 5 percent). Then, the method of reducing the data was to use the series resistance and the measured current-voltage curve to calculate dI/dV' as a function of V'. Extrapolation of the curve to $V' = 0$ yielded a value of $I_o e/AkT$; extrapolation to $V' = V_{oc}$ yielded a value of $I_o e/Akt \exp\left[(eV_{oc})/(AkT)\right]$. Simultaneous solution of these two equations yielded I_o and A.

The constants R_s, A, and I_o obtained by these calculations are shown in table I. The series resistance of the cell is considerably affected by the spectral quality of the light and decreases about 2 orders of magnitude when the light is changed from red to white. On the other hand, the reverse saturation current is little affected by a change in

TABLE I. - CONSTANTS DESCRIBING JUNCTION CHARACTERISTIC OF CADMIUM SULFIDE FILM CELL IN RED AND WHITE LIGHT

Light	Series resistance, R_S, ohm-cm^2	Reverse saturation current, I_o, A/cm^2	Dimensionless constant,[a] A
Red	56	7×10^{-5}	5.3
White	0.5	6×10^{-5}	3.4

[a]Equal to 1 for ideal junction.

the light. The constant A decreases by almost a factor of 2 from red to white light.

A simple interpretation of these results is that the CdS is highly photoconductive in green light but much less photoconductive in red light. In white light, the series resistance becomes 0.5 ohm-centimeter squared, and in red light the series resistance becomes 56 ohm-centimeters squared. The reason why the constant A is larger in red than in white light may be that a widened depletion region in red light causes a consequent increase in recombination losses. The widened depletion region is a result of the lower conductivity of the CdS in red light.

CONCLUDING REMARKS

The following explanation takes into account the observations of this study. Prior to heat treatment, cadmium sulfide (CdS) is unchanged from its original state in the evaporated film, and the resistance in the depletion region is low. The evaporated CdS layer is doped n-type with excess cadmium. Heat treatment produces diffusion of copper from the copper sulfide (Cu_2S) into the CdS. Copper is an acceptor in CdS so that compensation occurs, and the net carrier concentration in the CdS is reduced. This reduced carrier concentration increases the resistivity of the CdS, and, hence the series resistance of the cell. Consequently, short-circuit current and quantum yield decrease as a result of the heat treatment. Copper-doped evaporated layers of CdS are known to be highly photoconductive (ref. 6). Apparently, illumination of this photoconductive layer with red light produces some reduction in series resistance, but not a significant amount. Illumination of the photoconductive layer in the cell with green light reduces the cell series resistance considerably. Thus, the short-circuit current and quantum yield return to near their values before heat treatment. In summary, the effect of green secondary illumination on the spectral response of CdS film cells is ascribed to the photoconductivity of a copper-doped CdS layer in the region of the Cu_2S - CdS junction.

Basically, the preceding explanation is the same as that proposed by Shiozawa et al. (ref. 3). The experimental evidence presented in this report supoorts their explanation in every detail. It seems likely that photoconductivity of copper-doped CdS could also explain the observations of Cuong and Blair (ref. 4) concerning the spectral response of Cu - CdS barrier layer cells.

The photoconductive layer in the cell may control aspects of cell performance other than spectral response. It is well known that unprotected CdS cells deteriorate rapidly in moist air. This deterioration is generally reversible on thorough drying of the cell. Studies of the junction characteristic during moisture degradation show that the series resistance of the cell increases (ref. 7). Bube has observed that adsorbed water greatly lowers the photoconductivity of CdS crystals (ref. 8). It is conceivable that the effect of moisture on the cell is a result of a reduction of the photoconductivity of the copper-doped CdS layer by adsorbed water. Loss of photoconductivity in this layer will increase series resistance and decrease cell efficiency.

Lewis Research Center,
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