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NASA TN D-3849

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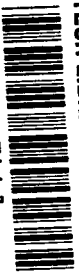
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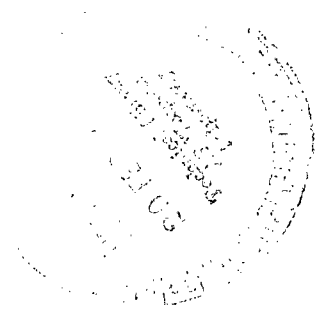
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

The cadmium sulfide film cell is a barrier-layer cell formed by a surface layer of chalcocite (Cu_2S) on cadmium sulfide (CdS). The chalcocite is a very degenerate p-type semiconductor with the Fermi level 1 to 3 electron volts below the valence band edge. The barrier height of the junction is about 0.85 electron volt. The spectral response of the cell in monochromatic light for photon energies greater than 2.4 electron volts (the blue response) is ascribed to direct excitation across the band gap of cadmium sulfide plus photoelectric emission from the barrier layer. The response for photon energies less than 2.4 electron volts (the red response) is ascribed solely to photoelectric emission from the chalcocite layer. The efficiency of this process is greatly affected by surface damage and surface impurities. After heat treatment, the spectral response can be altered by illuminating the cell with constant-intensity blue or red light during the spectral-response measurements. (This is not the case before heat treatment). This effect is ascribed to impurities in the cadmium sulfide introduced from the copper sulfide layer by the heat treatment.

INTRODUCTION

The photovoltaic effect in cadmium sulfide (CdS) was discovered by Reynolds in 1954 (ref. 1). Cells of single-crystal cadmium sulfide were produced with sunlight efficiencies up to 5 percent. Later, it was shown that evaporated polycrystalline films of cadmium sulfide could also be used to prepare solar cells (ref. 2). These early film cells were of low efficiency (~3.5 percent) but showed considerable promise in terms of low cost and light weight. Advances in film cell technology have resulted in 50-square-centimeter cells with conversion efficiencies of 5 percent (ref. 3). Shirland (ref. 4) has given a detailed history of the cadmium sulfide film cell. Much of the progress in cell technology has been made empirically. A thorough understanding of the cell mechanism should aid further advances in the efficiency of the cell. The research described in this report was performed to provide this understanding.
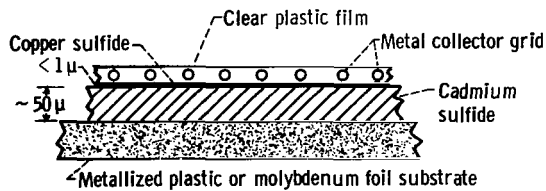
Figure 1. - Cross section of cadmium sulfide film cell.

A schematic cross section of the cadmium sulfide film cell is shown in figure 1. It consists of a layer of cadmium sulfide, 1 to 2 mils thick, on a metal foil or metallized plastic substrate, 1 to 2 mils thick, and a copper sulfide barrier layer, a few thousand angstroms thick, which is formed on the entire upper surface of the cadmium sulfide film. A fine copper- or gold-mesh collector grid is pressed to the copper sulfide layer. Leads are attached to the metal-foil substrate and to the collector grid, and the combination is laminated between two sheets of transparent plastic film. The cadmium sulfide layer is prepared by vacuum evaporation of cadmium sulfide onto a molybdenum foil substrate that is heated to a temperature of about 220° C during the deposition process. Heating the substrate is necessary to produce the correct electrical properties of the film. Impurities in the cadmium sulfide also affect the electrical properties of the film. General Electric luminescent grade cadmium sulfide sintered at 800° C for 72 hours in argon has proved to be the most suitable starting material. A standard procedure for forming the copper sulfide layer (refs. 5 and 6) is to etch the cadmium sulfide film briefly in acid, and then to dip it in a saturated aqueous solution of cuprous chloride for 5 seconds at 90° C. After the cell has been rinsed and dried, it is given a heat treatment in air. The heat treatment may vary from 30 minutes at 200° C to 2 minutes at 250° C. After the heat treatment, the cell is laminated in plastic. The efficiency of the cell is very sensitive to this process, and full efficiency is usually not achieved until after lamination has taken place.

CHARACTERIZATION OF COPPER SULFIDE BARRIER LAYER

The crystal structure of the copper sulfide layer on the surface of a commercial cell was examined by X-ray diffraction. A pattern characteristic of orthobombic-copper sulfide or chalcocite was found. In another experiment, an evaporated cadmium sulfide film was soaked in a hot cuprous chloride solution for several minutes to convert most of the cadmium sulfide to copper sulfide. The film was dried and scraped off. An X-ray powder pattern showed that the only species of copper sulfide detectable was chalcocite (Cu_2S). No trace of hexagonal copper sulfide, which has lattice spacings similar to cadmium sulfide, could be found, although earlier work with electron diffraction patterns of thin copper sulfide layers on cadmium sulfide (ref. 7) appeared to indicate the possible existence of hexagonal copper sulfide in the film.

The electrical properties of the copper sulfide layer were determined from Hall

coefficient and resistivity measurements. The sample was prepared by dipping a suitably masked high-resistivity single crystal of cadmium sulfide into a hot aqueous solution of cuprous chloride. Hall and resistivity measurements were performed on the copper sulfide film without removing it from the substrate. The depletion region produced in the cadmium sulfide provided effective insulation of the copper sulfide film from the cadmium sulfide crystal substrate. The handbook density of chalcocite, the area of the film, and the total amount of copper in the film as determined by quantitative analysis were used to estimate the thickness of the film. The Hall measurements showed copper sulfide to be p-type. Several films of copper sulfide were studied.

Calculated carrier concentrations ranged from 10^{20} to 10^{21} holes per cubic centimeter, and mobilities ranged from 1 to 10 square centimeters per volt-second. Cusano (ref. 5) had made similar measurements, with similar results, finding that the hole concentration is in excess of 10^{20} holes per cubic centimeter. A value of 3×10^{20} holes per cubic centimeter has been measured (private communication with E. R. Hill of the Harshaw Company, Cleveland). Such high carrier concentrations indicate that the copper sulfide layers are extremely degenerate and, in fact, must be more like a metal than a semiconductor. The Fermi levels in the copper sulfide layer were calculated by using the Sommerfeld approximate formula for extremely degenerate semiconductors (ref. 8). By assuming an effective mass of 0.1 for the holes, the Fermi level lies 0.8 electron volt below the valence band edge for a carrier concentration of 10^{20} holes per cubic centimeter and 4.0 electron volts below the valence band edge for a carrier concentration of 10^{21} holes per cubic centimeter at room temperature. The average of the two extreme values yields 2.4 ± 1.6 electron volts for the depth of the Fermi level in the copper sulfide layer.

A further property of the chalcocite required to complete the energy structure of this layer is the band gap. Marshall and Mitra (ref. 9) measured the optical properties of chalcocite and found the minimum energy gap to be 1.21 electron volts at 300° K.

JUNCTION BARRIER HEIGHT

The barrier height was measured in two ways: from the threshold for photoelectric emission, and from capacity-voltage plots.

Fowler plots (plots of the square root of quantum yield against photon energy) for a cell made from a single crystal and for a cell made from an evaporated film are shown in figure 2. Both the film cell and the single-crystal cell show straight-line portions, characteristic of photoelectric emission, that extrapolate to a threshold of 0.85 electron volt. The crystal cell was not heat treated; the film cell was. This value is the barrier height from the chalcocite side of the junction. The height from the cadmium sulfide side
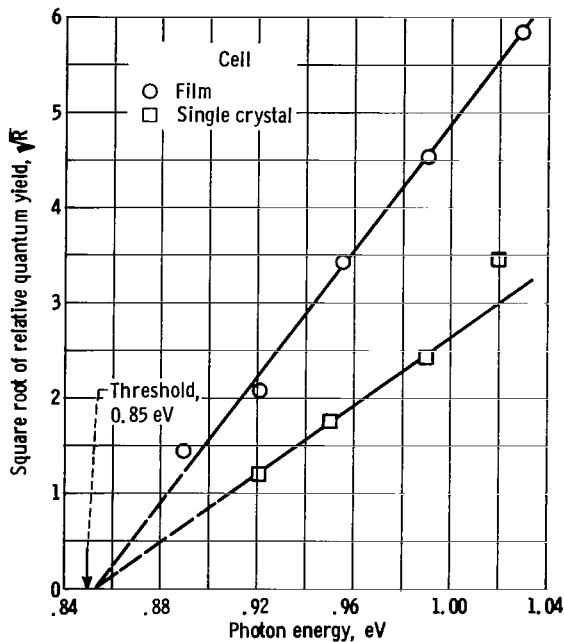
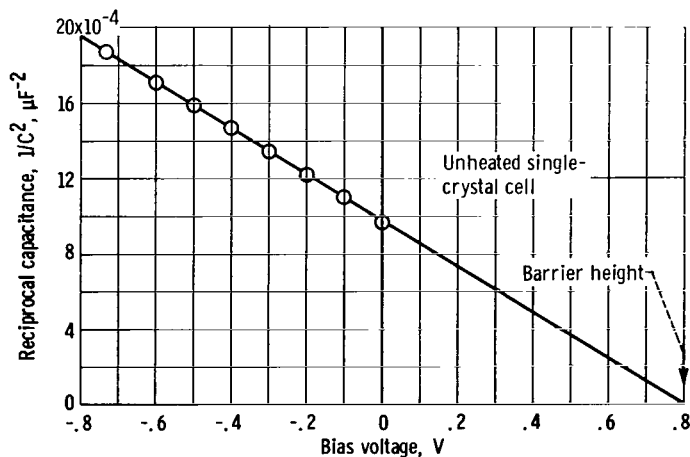Figure 2. - Fowler plots for cadmium sulfide film and crystal cells.

Figure 3. - Barrier height of cadmium sulfide-chalcocite junction from capacitance-voltage measurements for unheated single-crystal cell.

will be this value less the depth of the Fermi level in the cadmium sulfide. This height was estimated to be about 0.05 electron volt for both the crystal and the film, so that the barrier height from the cadmium sulfide side (the diffusion voltage) is about 0.80 electron volt.

Capacitance-voltage measurements were made on a number of film and single-crystal cells prepared in the conventional way. Plots of reciprocal capacitance squared against bias voltage were curved in all cases. Furthermore, the capacitance drifted slowly with time thus making measurements difficult or impossible. These effects were probably a result of impurity gradients and the presence of traps in the depletion region of the cadmium sulfide. In order to overcome this difficulty, cells were made from chemically polished single-crystal cadmium sulfide. No heat treatment was given the cell after the chalcocite layer was formed. (Chemical polishing was done by lapping the crystal with a cloth saturated with sodium hypochlorite solution). Cells made in this way gave linear plots of reciprocal capacitance squared as a function of bias voltage. Data for one of the cells are shown in figure 3. Extrapolation to zero yielded a barrier height of 0.80 electron volt, in agreement with the value from the photoelectric threshold.

Heat treatment and the state of the cadmium sulfide do not seem to affect the barrier height significantly, since the heat-treated film cell gave the same result as the unheated crystal cell. Heat treatment and the state of the cadmium sulfide, however, do affect the distribution of impurities and traps in the depletion region, as shown by the capacitance-voltage results.
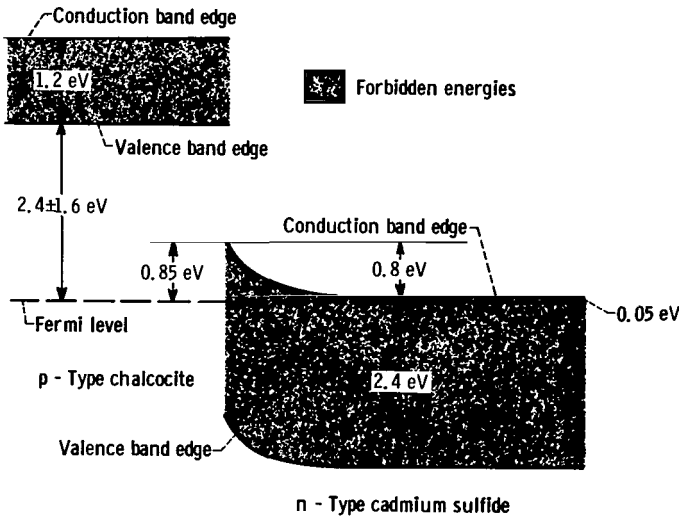

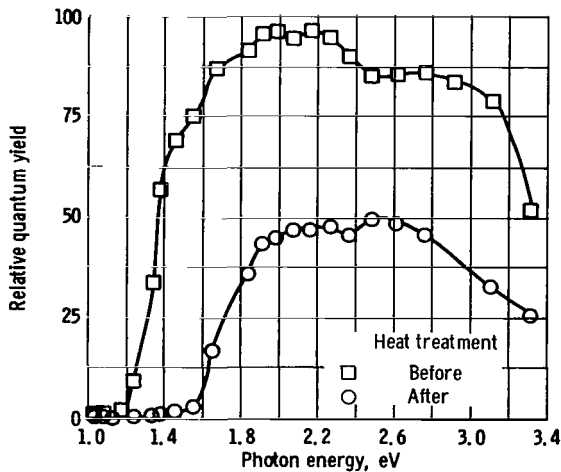Figure 4. - Energy band structure for cadmium sulfide-chalcocite photocell.

Figure 5. - Effect of heat treatment of barrier layer on monochromatic spectral response of cadmium sulfide cell. Heat treatment, 16 minutes at 220° C.

JUNCTION ENERGY BAND STRUCTURE

The information obtained about the various parts of the junction is assembled in figure 4. The junction is a barrier-layer type, and it does not differ in any basic way from the usual metal barrier-layer cell except that the barrier is unusually high and is equivalent to the height observed for platinum - cadmium sulfide barrier-layer junctions (ref. 10).

SPECTRAL RESPONSE OF CADMIUM SULFIDE CELL

The spectral response of the cadmium sulfide cell is unusual in two respects: (1) There is a large extrinsic response for photon energies less than 2.4 electron volts, the cadmium sulfide band gap. (2) The spectral response is present before heat treatment, but the effect of bias light does not appear until after heat treatment. In order to understand how the spectral response originates, it is helpful to discuss first the monochromatic response (absence of bias light) and then the bias light response.

Monochromatic Spectral Response

Figure 6. - Effect of surface treatment on monochromatic response of single-crystal cadmium sulfide cells. (Curves normalized to maximum response.)

The monochromatic response consists of two parts: the extrinsic, or red response from photons of energy less than the cadmium sulfide band gap, and the intrinsic, or blue response, from photons of energy greater than the cadmium sulfide band gap. The blue response certainly arises, in part, from electron-hole pair formation in the cadmium sulfide, a well-understood phenomenon. The origin of the red response is more difficult to understand.

Heat treatment of the barrier layer does not appear to have any basic effect on the nature of the monochromatic red response. This can be seen in figure 5, where no new response maximums or minimums appear after heat treatment. However, heat treatment does affect the size of the red response relative to the blue response. This is characteristic of the red response, in that its magnitude relative to the blue response is sensitive to many different treatments of the surface. Figure 6 shows the effects of various surface treatments on the red response of single-crystal cells. Figure 7 shows the effect of annealing the evaporated cadmium sulfide film on the red response.
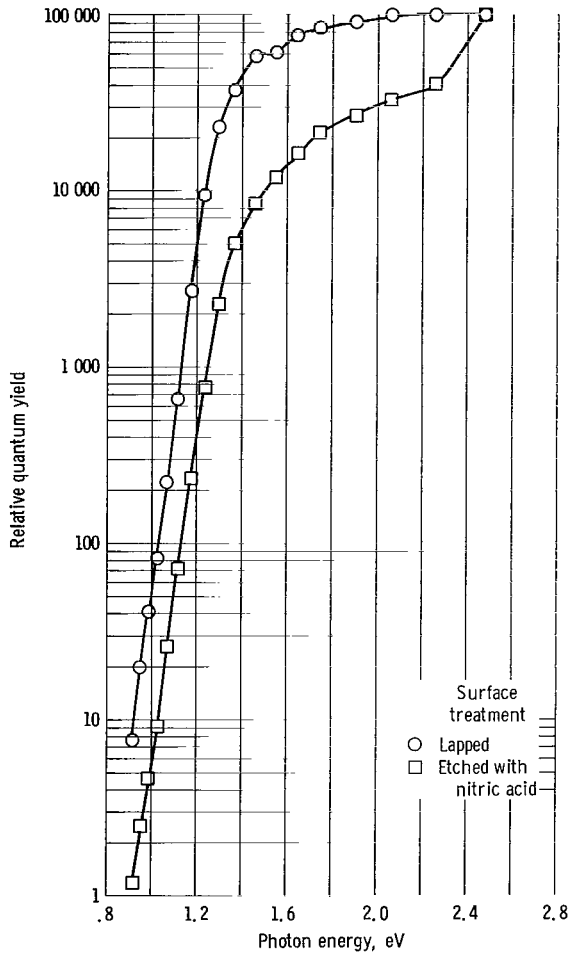
Figure 8 shows that the red response can be influenced by the diffusion of metal into the surface of the cadmium sulfide film. In order to interpret these results, it is necessary to know the origin of the red response. There are only two possibilities. It may arise either from photoelectric emission from the copper sulfide or from impurities in the cadmium sulfide. Photoelectric emission is certainly responsible for some of the
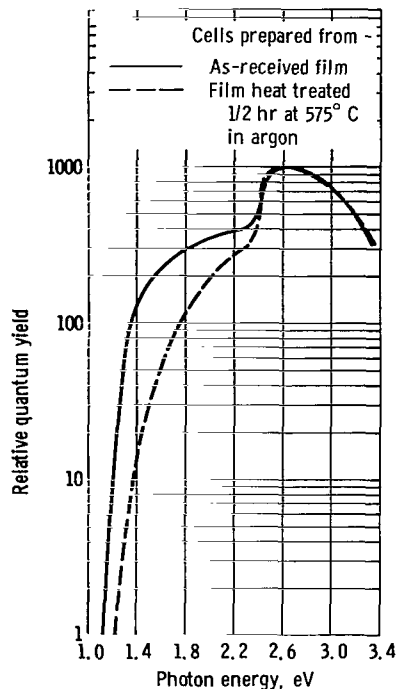
Figure 7. - Effect of annealing cadmium sulfide film on red response of film cells. (Curves normalized to maximum response.)
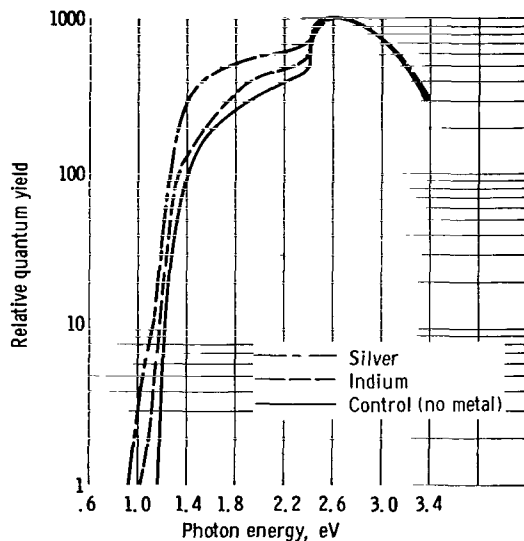

Figure 8. - Metals diffused into cadmium sulfide film increase red response of cadmium sulfide cells. Thickness of metal covering, 200 angstroms; heat treatment, 575° C; length of treatment, 5 minutes.

red response. As shown in a previous section, the photoelectric response near the red threshold varies with photon energy in a way characteristic of photoelectric emission. Monochromatic response from impurities in the cadmium sulfide is conceivable. An impurity center below the Fermi level may have attached to it an electron that can be excited to the conduction band by absorption of a photon. In order to get a net current flow through the junction, the excited electron must be replaced from somewhere other than the conduction band. Replacement can occur by transfer from an adjacent impurity center or by tunneling through the barrier from the copper sulfide. Ruling out these processes is difficult especially in films that contain high impurity concentrations. Qualitative evidence against monochromatic impurity response in the cadmium sulfide cell is as follows: A cell was prepared from a high-purity single crystal of cadmium sulfide ($n = 10^{16}$ electrons/cm^3, Hall mobility = 100 cm^2/(V)(sec)). No heat treatment was given the cell. It seemed unlikely that this cell could show any substantial impurity response. The spectral response of this cell is compared with the responses of a number of other cells in figure 9. The coordinates used in this figure were chosen to show the region of linearity of the Fowler plot. (For photoelectric emission near the threshold, the square root of the photoelectric current is directly proportional to the photon energy less the threshold photon energy. Consequently, a log-log plot of the square root of the photoelectric current against the photon energy above threshold will be a straight line with a slope of 1 in the region characteristic of photoelectric emission near the threshold). Spectral responses for some of the cells in this figure were taken from figures 7 and 8. In addition to the high-purity
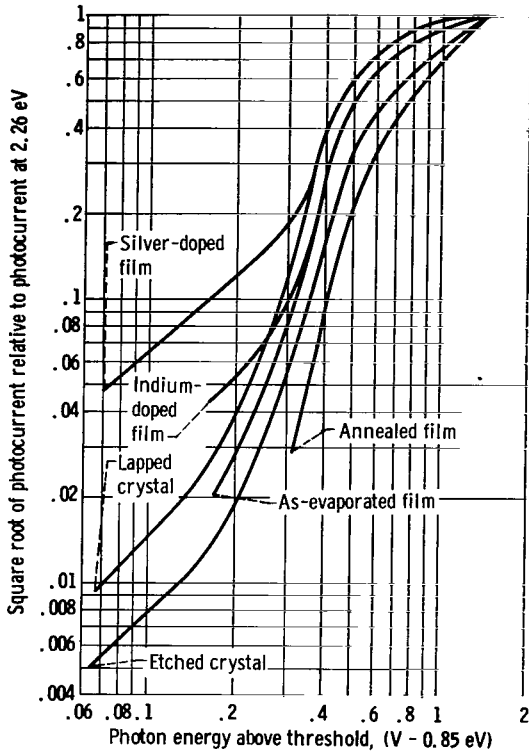
Figure 9. – Effect of various treatments on red response of cadmium sulfide-chalcocite cells.

single-crystal cell, data are shown for cells made from an as-evaporated film, an annealed film (1/2 hr at 575° C in argon), a silver-doped and an indium-doped film (doping was performed by evaporation of 200 Å of the metal on the surface of the film, followed by a 5-min heat treatment in argon at 575° C), and a lapped single crystal. All cells made from films were heat treated; the lapped single-crystal cell was not. The effect of lapping the single-crystal surface is to increase the red response uniformly above that of the unlapped crystal. The response from the as-evaporated film lies between the lapped and unlapped crystals. The effect of annealing the film is to decrease the red response uniformly. Metal doping appears to increase the red response in the low energy part of the response. In no case, however, do any new features of the response emerge. The red response of the heat-treated film cells is qualitatively the same as the response of the unheated cell made from a high-purity single crystal. If impurities in the cadmium sulfide films are responsible for some of the monochromatic red response, it would be expected that some new feature would appear in this comparison. None does. Tentatively, it is concluded that photoelectric emission is the major process that provides the monochomatic red response of the cell. The data in figure 9 do show that the red response is very sensitive to the nature of the cadmium sulfide surface. This result can be interpreted to mean that the collection efficiency for electrons photoemitted across the barrier is sensitive to the state of the barrier interface. Evidently, indium and silver doping and lapping promote a high efficiency; whereas, annealing promotes a low efficiency.

One effect of lapping is to produce a darker surface layer on the crystal of higher conductivity than the bulk crystal. This layer probably contains excess cadmium because of the decomposition of cadmium sulfide by local heating resulting from the abrasive process. Thus, the effect of both metal doping and lapping is to produce a highly doped surface layer. The as-evaporated film owes its high conductivity to excess cadmium (refs. 11 and 12), which can be removed by annealing (ref. 12). The annealed films display a considerably lower red response than the as-evaporated films.

Thus, it appears that high efficiency for the photoelectric emission process is associated with high conductivity in the surface of the cadmium sulfide. The effect of

8

Relative quantum yield

100
90
80
70
60
50
40
30
20
10
0

Photon energy, eV
1.0   1.4   1.8   2.2   2.6   3.0   3.4

O Before treatment with hydrogen sulfide
□ Immediately after treatment with hydrogen sulfide
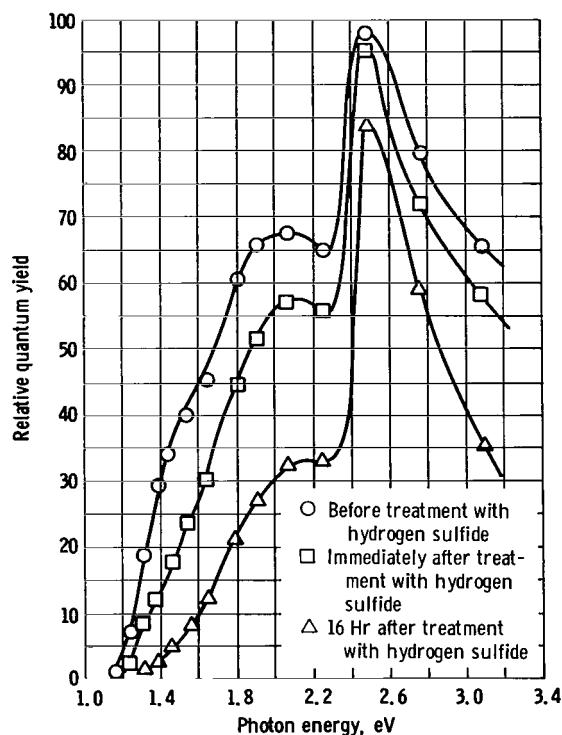△ 16 Hr after treatment with hydrogen sulfide

Figure 10. - Effect of hydrogen sulfide on spectral response of cadmium sulfide film cell.

hydrogen sulfide on the red response can be explained in terms of the spectral response curves in figure 10. Hydrogen sulfide reduces the overall response but, the red response is decreased considerably relative to the blue response. Because the evaporated cadmium sulfide film owes its conductivity to excess cadmium, the effect of hydrogen sulfide is probably to remove excess cadmium by chemical reaction and, hence, reduce the conductivity at the cadmium sulfide film surface. This reduced conductivity results in a lower efficiency for the photoelectric emission which, in turn, produces the red response.

It is reasonable to speculate that the conductivity of the cadmium sulfide determines the current yield from photoelectric emission because of the width of the depletion region. The width of the depletion region is inversely proportional to the conductivity of the cadmium sulfide. Since the barrier height is constant, the electric field in the depletion region increases as the width of this region decreases. Both these factors reduce the time spent by an electron in the depletion region, and, consequently, reduce the probability of recombination in the depletion region.

Since an improved red response is desirable, it might appear that the cadmium sulfide surface should be doped as heavily as possible to reduce the depletion region width to as small a value as possible. This is not the case, however, because, as the depletion width is decreased, tunneling lowers the effective barrier height. This reduced barrier height reduces the open-circuit voltage of the cell, and, consequently, its sunlight efficiency. Evidently, a doping level corresponding to an optimum depletion region width exists.

SPECTRAL RESPONSE WITH BIAS LIGHT

The effect of bias light is complex. At least two different effects are seen for cells prepared by the standard dipping process. One effect is an enhancement of the red response by blue bias light (fig. 11), and the other is an enhancement of the blue response by red bias light (fig. 12). These effects are probably the result of impurities and
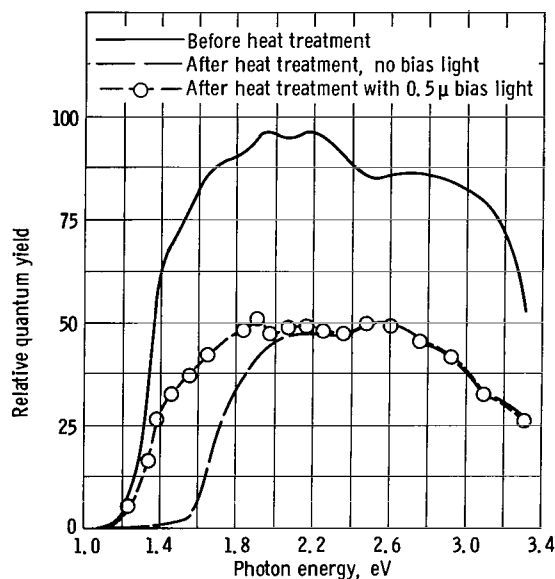
Figure 11. - Enhancement of red response of cadmium sulfide cell by blue bias light. Heat treatment, 16 minutes at 220° C.
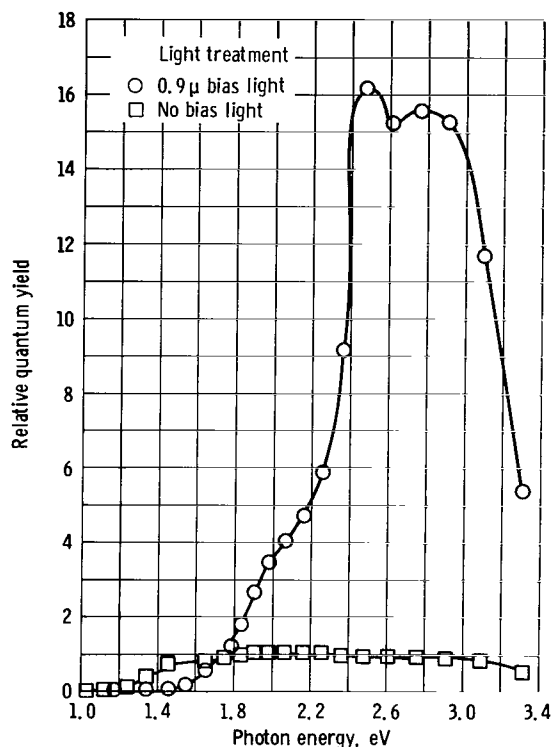

Figure 12. - Enhancement of blue response of cadmium sulfide cell by red bias light. Cell heat treatment, $3\frac{1}{2}$ minutes at 220° C.

imperfections in the depletion region of the cadmium sulfide, since they are not present before heat treatment of the cell. Heat treatment will cause copper to diffuse into the cadmium sulfide from the copper sulfide. The chloride ion is always present in the copper sulfide layer, and it may also diffuse into the cadmium sulfide on heat treatment. Other less obvious impurities, such as the hydrogen ion, may be important.

The enhancement of red response by blue bias light is illustrated in figure 11. In general, the blue light seems to restore the red response to its original response (before heat treatment). No new response peaks are produced by the blue bias light. Since photons with energies greater than the band gap of cadmium sulfide are required to produce this effect, it appears that holes are the carriers active in causing the red enhancement. The implication here then is that an acceptor impurity such as copper is responsible. Since no new peaks are produced by the blue bias light, the acceptor impurity must produce a general lowering of photoelectric emission efficiency. The capture of holes by the acceptor impurity neutralizes this effect. Further experiments are required to clarify this explanation completely. A somewhat similar effect has been observed by Cuong and Blair (ref. 13), who reported a peak in the red response that was ascribed to a response from copper impurities.

The enhancement of the blue response by red bias light, as illustrated in figure 12, is a very puzzling effect. Electrons produced by photoelectric emission seem to be stored in the cell eventually to be released by blue light. No explanation for this effect is offered at this time.

CONCLUDING REMARKS

The cadmium sulfide film cell is a barrier-layer photocell in which highly degenerate copper sulfide is the barrier-layer material. The barrier height from the Fermi level in the copper sulfide is about 0.85 electron volt. The red response of the cell is the result of photoelectric emission from the copper sulfide into the cadmium sulfide. The blue response comes partly from photoelectric emission and partly from intrinsic absorption of photons by the cadmium sulfide. The efficiency of photoelectric emission (and, consequently, the sunlight conversion efficiency) is largely controlled by impurities in the cadmium sulfide near the junction. For example, before heat treatment, the spectral response of the cell is not affected by secondary illumination. After heat treatment, it is. This effect on spectral response is probably a result of diffusion of impurities from the chalcocite layer into the cadmium sulfide.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, October 21, 1966,
            120-33-01-02-22.

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—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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