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Cadmium sulfide (CdS) thin film solar cells have come a long way in the past several years and now look promising. Currently being made are 4 to 7 percent efficient 3X3 inch cells with 8 to 10 percent cells not an unrealistic goal in the future. When one begins to consider arrays for space power systems, the necessity of assigning performance parameters to the cells becomes apparent. As a result, the stability of the thin film cells has come under closer scrutiny in recent months.

First, we will consider our experience at NASA Lewis Research Center on the storage stability, moisture degradation, and thermal cycling durability. Secondly, we will deal with some aspects of the mechanism for the CdS-Cu_2S solar cell.

The cells that we are concerned with have a thin metal or plastic substrate (1 or 2 mils thick) on which is deposited a mil of CdS, then a barrier of Cu_2S, a gold (Au) or copper (Cu) current collecting grid, and finally the adhesive and encapsulating plastic of either Mylar or H-film. The solar cell is 3X3 inches and about 5 mils thick. It is very flexible, light, and shows no sign of wear or damage as a result of normal handling. However, the cells do appear to degrade during storage in a double desiccator under ambient conditions or in a vacuum desiccator. Figure 1 shows the efficiency of several types of CdS cells as a function of the time in storage. The data presented are averages from more than 120 cells. The gold-gridded cells (solid lines) that depend on the pressure of the encapsulating plastic to hold the grid in contact with the barrier are quite stable, degrading about 0.1 percent every two months. The cells having the Au grids electroplated directly onto the barrier show no degradation with time, however the electroplating process reduces the power output of the cell. The copper-gridded cells (dotted lines) that depend on the pressure of the encapsulating Mylar to hold them in place degrade very rapidly but do reach a stable condition in 3 to 7 weeks. The Cu-gridded cells (dashed lines) that depend on the pressure of the H-film to hold them in place degrade slower and reach a stable condition in 2 to 6 weeks. The Au-gridded cells are quite satisfactory except for the cost of the grid, which is approximately $8 per cell. To lower this cost, one manufacturer has switched to Cu grids. The drop in efficiency for these cells is because of an increase of the series resistance due to the grid lifting from the barrier of the cell. Some of this current loss can be recovered by the application of pressure to the cell package while relamination usually results in a completely recovered cell. The voltage remains virtually unchanged.

It thus appears that the storage-stability problems occur because the grids do not maintain good contact with the barriers. The movement of the grid can result from the release of stresses built up in the cell during lamination. Since the grid becomes an integral part of the adhesive and plastic, it must either move or be deformed as the stresses are relieved. The more ductile Au grid can deform more easily than can the Cu, which would transfer the stress directly to the grid-barrier interface. Approaches to the problem now being evaluated include improved lamination conditions and epoxy cements to hold the grids in place. Proper annealing of the laminated cell

may be another approach to the problem.

Moisture degradation of CdS cells has been a long standing problem. The extent of the problem is shown in figure 2 where the percent degradation of the maximum power per day is plotted as a function of the relative humidity. Both 1- and 2-mil Mylar and H-film encapsulated cells are plotted. Although at 100-percent relative humidity the cell's life is very short, the rate of degradation could be tolerated at low humidities. More will be said on this later.

A detailed study was made at 65-percent relative humidity. In figure 3 the decrease of both the short-circuit current and the open-circuit voltage is shown as a function of time. The tests were made in humid air at ambient temperature and pressure. It is of interest to note that during the first month or so the current decreased rapidly before leveling off while the voltage decreased only slowly. In figure 4 the series resistance R_s and the saturation current I_o are plotted as a function of time. Both the R_s and I_o increase very slowly for the first month then rapidly increase. The shunt resistance decreased during the first month, then tended to level off. The spectral response of the cells from 0.4 to 1.1 u decreased uniformly during the first month. Later the intensities were too low for accurate measurements, although there was an indication that the red response was affected.

From these data we concluded that water penetrates the cell's plastic cover and is adsorbed in the junction thus increasing the number of recombination centers so that the current is reduced. No permanent damage is done to the junction, at least initially. It was also found that if the degraded cells were heated in a vacuum, a portion of the lost current could be restored, whereas pressure alone had no effect. (This is in contrast with the storage degradation where pressure alone did restore some of the current.) Thus, as mentioned earlier, low rates of degradation might be tolerated, since once in space the cells can be expected to recover at least a part of their lost power as they are heated by the sun.

The most stringent tests and probably the most important for space applications are the thermal cycling tests being run at Lewis. In table I the main features of the two thermal cycling facilities now in use are listed. Currently, solar cells are subjected to a series of thermal cycles consisting of 15 minutes of light and 15 minutes of darkness. The data, consisting of temperature, open circuit voltage V_{oc}, and four load currents, are automatically recorded when the cells approach equilibrium temperature. During the dark portion of the cycle, the cells are cooled to the temperature range of -90° to -120° C. In the simulated sunlight, cells reach a temperature of 0° to 100° C depending on the intensity of the light. Light intensities of 100 to 200 mw/cm² have been used for these tests. When this program began almost 2 years ago cells barely lasted 10 cycles, but progress has been steady and today we have cells that have not lost any of their original performance after 2,000, 4,000 and even 10,000 thermal cycles.

In figure 5 typical thermal cycling data are shown where the relative power output is plotted against the number of thermal cycles. All cells that depended on pressure alone to hold the grids in place (Au or Cu) failed in the manner shown. Some failed very soon and others after thousands of cycles but all failed in the same way. They developed short circuits as a result of the movement of the grid across the barrier during the thermal cycle. The shorts can be removed in most cases by buring them out, by relamination, or simply by annealing them. Epoxy-cemented grids failed because the epoxy did not bond to the grids. The best metal substrate cells are those where the Au grids are electroplated directly onto the barrier. They have stood up very well in thermal cycling. The front-wall plastic-substrate cells have also successfully withstood thermal cycling. One of these cells has shown almost no drop in power

output after 10,000 cycles. The thermal cycling tests have uncovered many defects in thin-film cell construction. However, subsequent cells have proved to be much more reliable and, as improved film cells are developed, we shall continue to evaluate them in these simulated space chambers.

Another of the problems of this cell is that we do not understand very well how it works. Improvements in the cell have been made empirically for the most part. If we can make some progress in understanding the cell, this may help to improve the present cell and may possibly point the way to new types of cells.

To begin with, it is necessary to characterize the copper sulfide layer as completely as possible. Table II shows the results of our study of the crystal structure of the chemically formed copper sulfide layer. First of all electron diffraction was used to examine thin layers of the sulfide formed on single crystal CdS. It was found that the copper-sulfide film had a hexagonal structure with lattice spacings only a few percent different from CdS. This corresponds to a high T modification of Cu_2S, which is normally stable only down to 105° C. Thicker films of the copper sulfide, when examined by X-ray diffraction show the film to be orthorhombic Cu_2S or chalcocite. Thus, the film is composed of Cu_2S with a crystal structure that closely matches the CdS structure at the interface. Further from the interface, the stable chalcocite form of Cu_2S is predominate. Since the crystal structures of the Cu_2S and CdS are similar at the junction, we expect a minimum number of imperfections at the interface. This may explain the high light-generated current in this cell.

We have learned three basic electrical properties of the copper sulfide layer. It is p-type. From Hall-coefficient measurements on the film we have found that the carrier concentrations are in the range of 10^{21} carriers/cm^3. Hence, the material is degenerate. We have measured the optical absorption coefficient of the film as a function of the wavelength and, after correcting for the free carrier absorption, we find that the optical band edge is clearly defined and corresponds to a band gap of 0.9 eV.

Since we know something about the properties of the copper sulfide, it is possible to sketch the band structure for the cell. This is done in figure 6. The barrier height of 0.8 eV shown in the figure was determined by capacity-voltage measurements. Nearly all of the band-bending occurs in the CdS, due to the high carrier concentration in the Cu_2S.

Now we would like to consider what might be expected for the spectral response of this heterojunction as a photovoltaic device. We should expect that the cell would begin to yield current from red light at an energy near 0.9 eV, the Cu_2S band gap. We should also expect to see an increase in the photocurrent when the photon energy reaches the band gap of CdS at 2.4 eV. Figure 7 shows the spectral response of a CdS film cell. The spectral response shown here are all relative to the maximum response at around 2.6 eV. No bias or green light was used. The expected increase in photocurrent at 2.4 eV occurs, but the threshold energy for the cell is about 1.2 eV rather than the expected 0.9 eV. It should be mentioned that the magnitude of the red response of the cells (the response from 1.2 to 2.4 eV) is quite variable, depending on how the cell is made. More will be said about this later. However, for a typical CdS film, the threshold remains at about 1.2 eV. This result suggests that the red response in the cell does not originate in the Cu_2S layer. The other possibility is that it arises from deep impurity levels in the CdS located at an energy depth of about 1.2 eV.

We next tried to identify the impurity. After considering several possibilities, we have come to the tentative conclusion that the impurity responsible for the red

response in the cell is excess cadmium. Evaporated CdS films are known to be non-stoichometric and recent work has shown that they contain excess Cd. It has also been shown that some of the excess Cd can be evaporated out of the film by heat treatment. Hence, we expect that heat treatment of a film should lower the red response, if Cd is responsible. We took two nominally identical CdS films, both from the same evaporation, and heated one in argon for 1/2 hour at 575° C. We then made cells from both films. The results are shown in figure 8. The red response of the heated film is lowered considerably. This experiment was repeated several times with identical results. In a second experiment, we investigated the effect of putting Cd into the films. Two identical films were heattreated to remove some of the excess Cd. One of the two was coated with a thin film of Cd metal and again heated briefly. The red response of the cell made from the Cd-treated film was higher than the untreated cell. This is again evidence that excess Cd is in some way responsible for the red response.

A third experiment was performed by exposing the cell to hydrogen sulfide. We expect H_2S to react chemically with the excess Cd thereby removing it. Cell performance degrades rapidly on exposure to H_2S. Spectral-response measurements of slightly degraded cells showed a considerable loss of red response, which can be explained by the removal of free Cd. We conclude from these three experiments that the red response of the cell is largely due to excess Cd in the lattice.

We then became interested in the possibility that other metals besides Cd might be used to produce deep donor impurities. Silver (Ag) and indium (In) are adjacent to Cd in the periodic table and have similar sizes. Therefore, we expect that they might enter the CdS lattice in a way similar to Cd. Figure 9 shows the effect of introducing these metals into CdS films. Both In and Ag increased the red response of the cells.

In summary, the major problem areas associated with the CdS film cells are storage, humidity, thermal cycling and mechanism. The storage stability problem can be eliminated by the use of grids that are firmly attached to the cell. For humidity damage, we find that the cells can be exposed to 20-percent relative humidity for long periods of time (i.e., long enough to assemble an array with little or no damage). By proper construction methods, film cells that are very resistant to thermal cycling can be made. Plastic substrate and electroplated-grid cells have been made that can withstand 10,000 cycles, which is equivalent to 2 years in Earth orbit. As to the mechanism of the cells, they appear to be heterojunctions of CdS and Cu_2S, with the red response of the cell due to excess cadmium in the film. Possibly, better control of the Cd content or the use of other metals may improve the cell.

Table I. - THERMAL CYCLING FACILITIES

	NO. 1	NO. 2
Tank size	10-in. diam by 26-in.	30-in. diam. by 4-ft.
Pumping system	8 in. D.P.	10 in. D.P.
Min. Pressure, Torr	10^{-5}	10^{-7}
Cooling medium	LN_2	LN_2
No. of solar cells (3 in. by 3 in.)	4	25
Solar simulation, watts	7 - 600 sun guns	5 KW Xenon 900 tungsten

TABLE II. - CRYSTAL STRUCTURE OF COPPER SULFIDE BARRIER LAYER

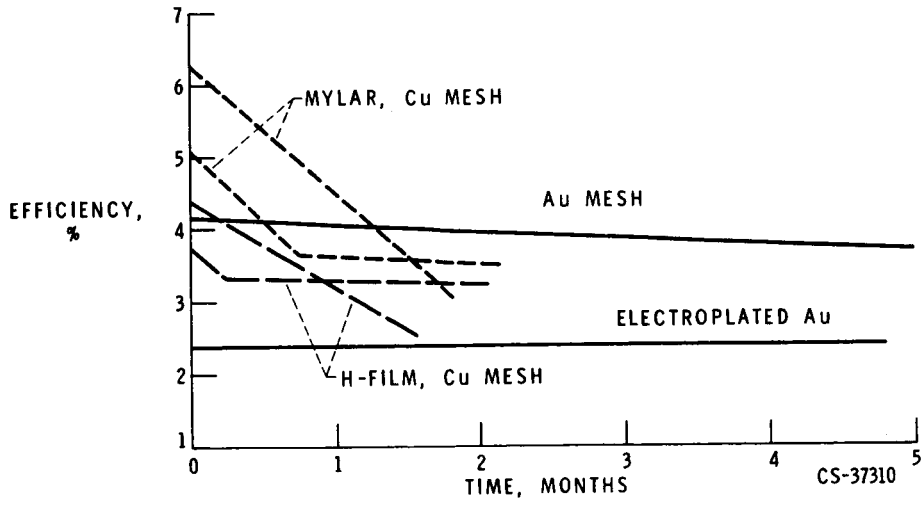| Technique	Result
Electron Diffraction (Thin Layer)	Cu_2S, Hexagonal, High Temp Modification, Close Match to CdS Lattice
X-ray Transmission	Cu_2S, Orthorhombic (Chalcocite)

STORAGE STABILITY OF CdS SOLAR CELLS

Figure 1.

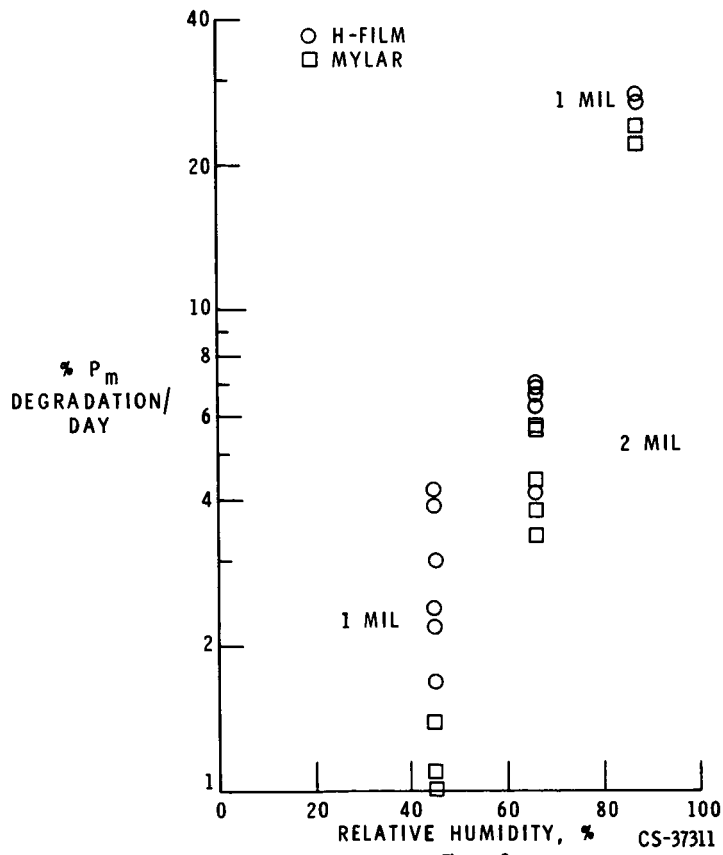## DEGRADATION RATE OF MAXIMUM POWER

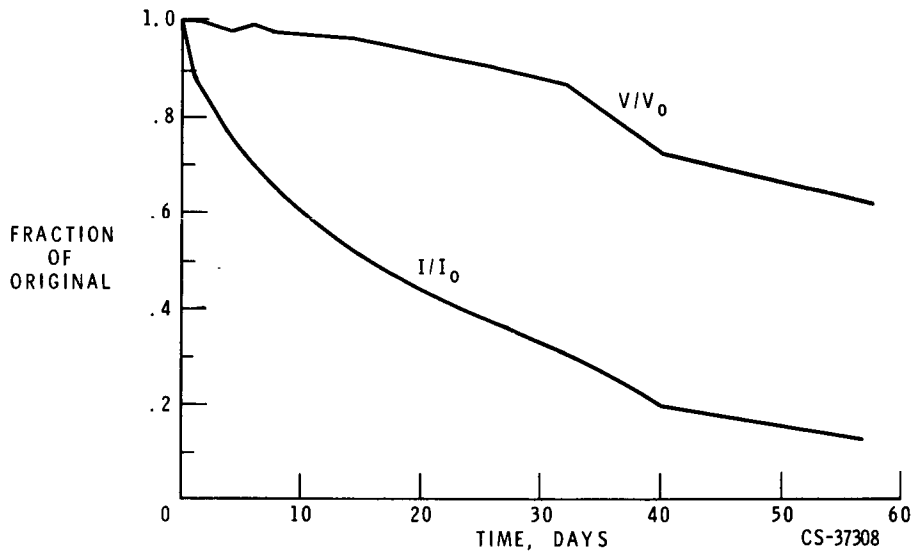Figure 2.

DEGRADATION OF V_{OC} AND I_{SC} BY MOISTURE
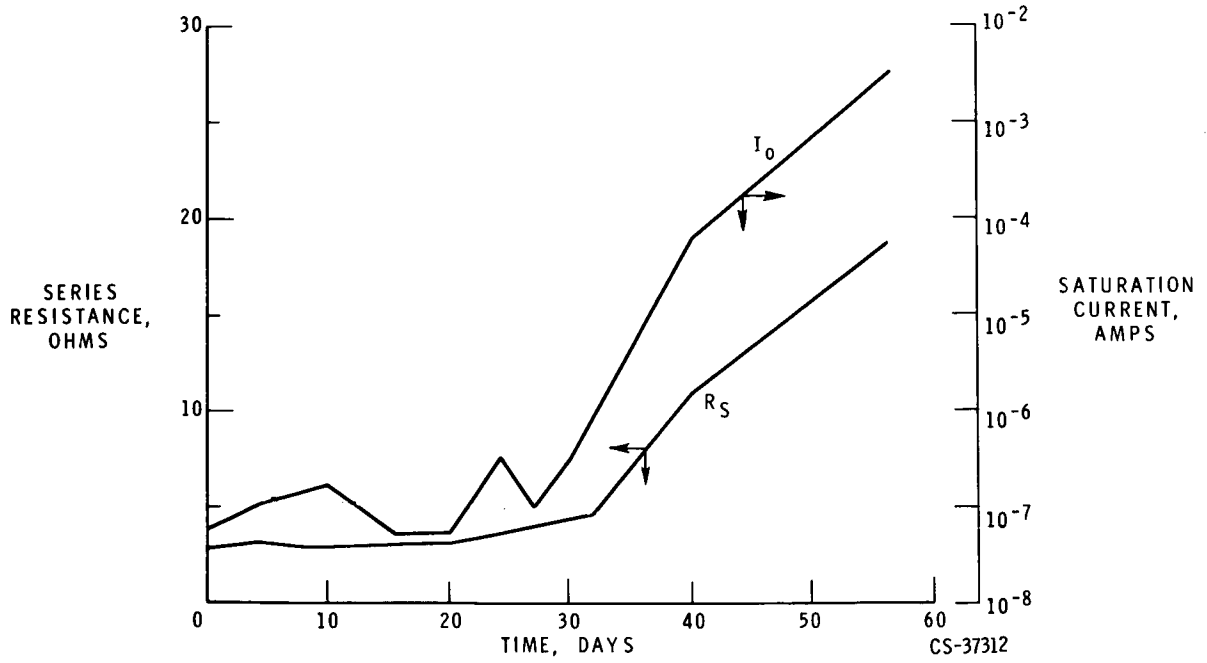

Figure 3.

EFFECT OF MOISTURE ON R_S AND I_O
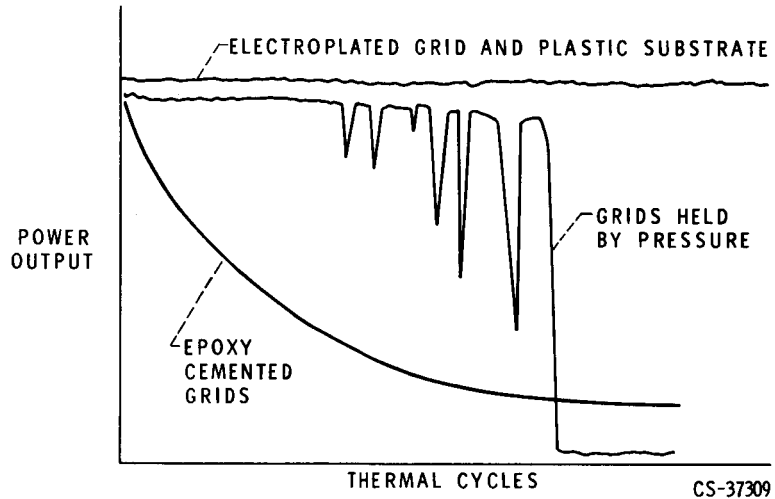

Figure 4.

THERMAL CYCLING OF CdS SOLAR CELLS

POWER OUTPUT

ELECTROPLATED GRID AND PLASTIC SUBSTRATE

GRIDS HELD BY PRESSURE

EPOXY CEMENTED GRIDS

THERMAL CYCLES

CS-37309

Figure 5.

ENERGY BAND STRUCTURE FOR CdS FILM CELL

0.9 eV

0.8 eV

Cu_2S

FERMI LEVEL

2.4 eV

CdS

CS-37318
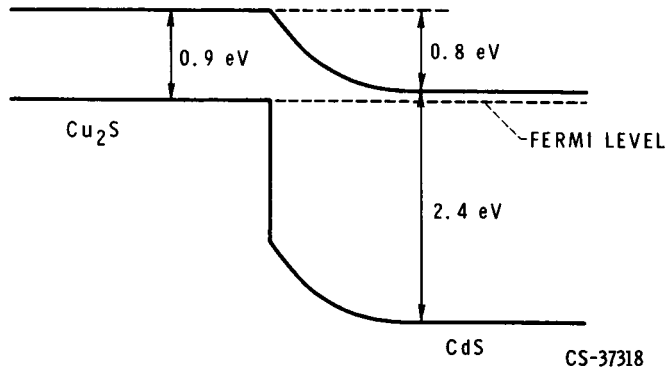
Figure 6.

SPECTRAL RESPONSE OF TYPICAL CdS FILM CELL
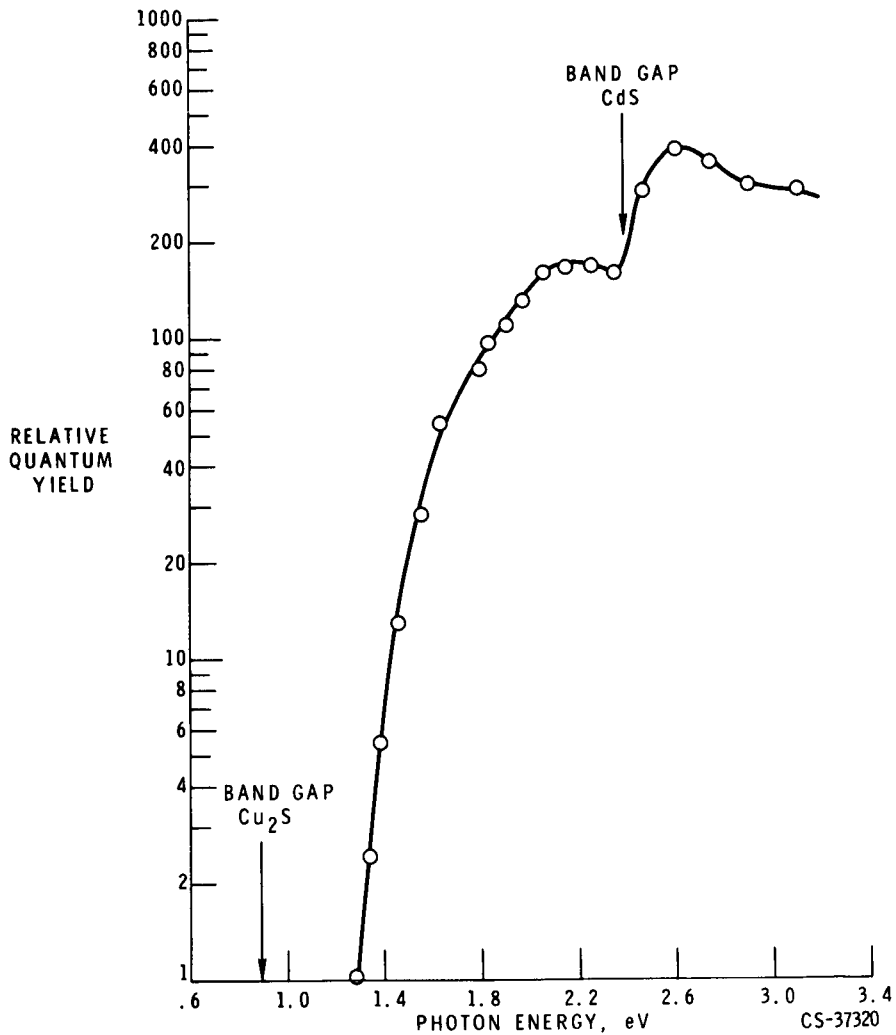
Figure 7.

REMOVAL OF EXCESS CADMIUM REDUCES RED RESPONSE OF CdS CELLS

CELL PREPARED FROM
AS-EVAPORATED
FILM

CdS
BAND GAP

RELATIVE
QUANTUM
YIELD

CELL PREPARED FROM
FILM HEAT-TREATED TO
REMOVE EXCESS CADMIUM

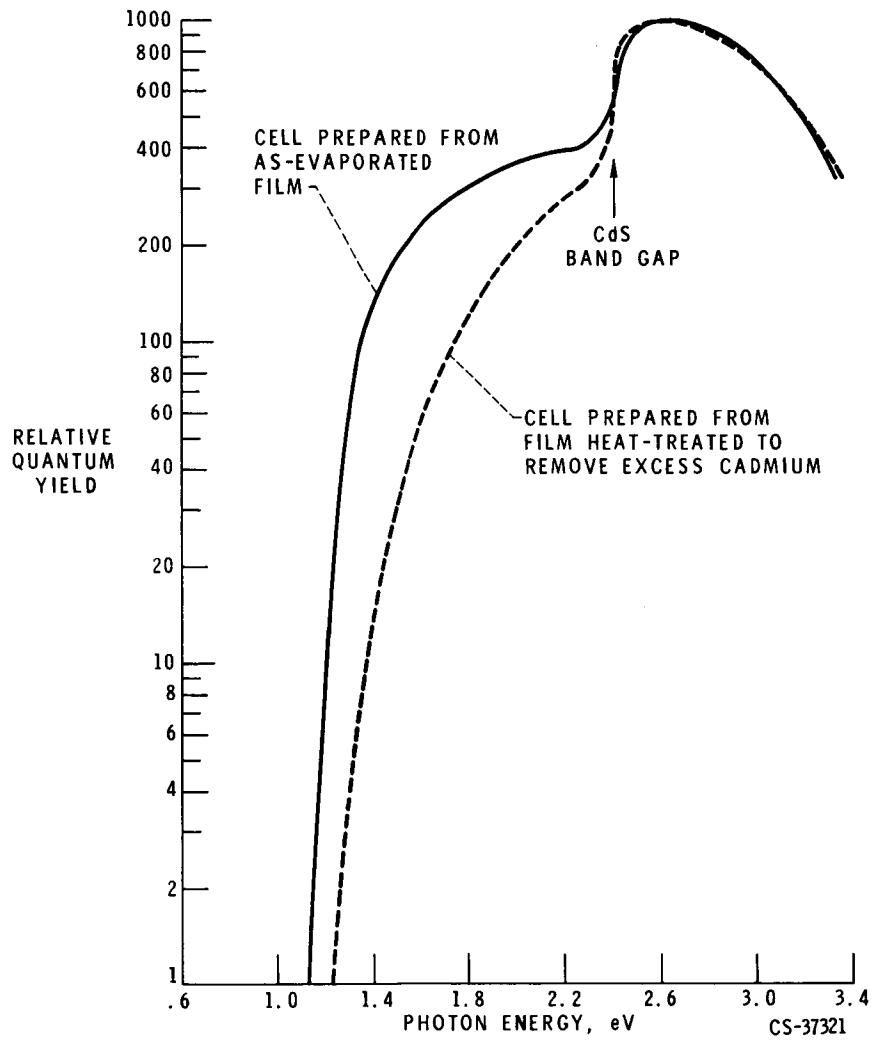PHOTON ENERGY, eV

CS-37321

Figure 8.

METALS DIFFUSED INTO CdS FILM INCREASE RED RESPONSE OF CdS CELLS

Figure 9.