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THE PERFORMANCE OF THIN FILM SOLAR CELLS EMPLOYING PHOTOVOLTAIC Cu_{2-x}Te - CdTe HETEROJUNCTIONS ⁽¹⁾

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Résumé. — Bref rapport sur le perfectionnement des cellules solaires à couches minces de Cu_{2-x}Te - CdTe en vue des applications aéro-spaciales. On décrit la fabrication et les caractéristiques de fonctionnement ainsi que la conservation à terre, la stabilité lors des cycles thermiques et la résistance aux radiations. On effectue des expériences avec des jonctions de cristaux uniques comme base d'étude des jonctions Cu_{2-x}Te - CdTe , et pour orienter le travail sur les couches minces. Le problème le plus urgent est d'accroître la durée de vie de la cellule, en particulier aux températures élevées.

Abstract. — This paper is a short status report on the continuing development of Cu_{2-x}Te - CdTe thin film solar cells for eventual aerospace application. The fabrication and operating characteristics are described, as well as on-earth maintenance, stability to thermal cycling, and resistance to radiation. Experiments with single crystal junctions are used to obtain a basic understanding of the Cu_{2-x}Te - CdTe junctions, and to guide future thin film work. The most pressing current need is to determine how to extend cell life, particularly at elevated temperatures.

The General Electric Company has had a continuous effort on thin film solar cells for the past four and a half years. The work has been devoted primarily to exploring thin film CdTe as a possible substitute for single crystal silicon in meeting future requirements of aerospace vehicles. The potential advantages of thin film cells are well known. The main ones are 1) high power-to-weight ratio, 2) low cost in large arrays, and 3) high radiation resistance. Semiconducting CdTe , with a direct band gap of 1.45 eV at room temperature, is near the theoretical optimum for conversion of solar energy by the intrinsic photovoltaic effect. This directness of energy gap gives rise to large absorption coefficients, which means that most of the absorption of the solar radiation occurs in a distance of the order of a micron or so. This then implies that in a comparison to single crystal silicon, 1) thinner cells are possible and with higher power-to-weight ratios and lower degradation rates to penetrating radiation and 2) shorter minority carrier lifetimes are permitted. Low lifetimes are characteristic of most thin films.

This paper will first describe the thin film construction, then briefly the method of preparation, follow this with a report of some of the operating characteristics, and then discuss some of the information obtained from single crystal studies. Figure 1 exhibits the thin film construction. A low

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FIG. 1. — Cross section of a Cu_{2-x}Te - CdTe thin film solar cell.

resistivity n -type CdTe layer approximately 10 microns thick is deposited on a 1 or 2 mil molybdenum foil. It has been found that an interposed thin film of highly doped n -type CdS about 0.5 to 1.0 microns thick aids considerably in achieving non-rectifying contact between the metal foil and the n -type CdTe base layer. To assure an optimum photovoltaic effect, the resistivity of the CdTe region within a micron or two of the top surface is modified by counterdoping with acceptor-type impurities. It is in this region that the major production of electron-hole pairs takes place and where it is also expected that they subsequently separate. At the surface of this modified region a cuprous telluride layer is reaction grown by placing the sheet for 8 to 12 seconds into an aqueous cuprous ion solution at about 85 °C. Cadmium goes into solution and copper replaces it to form copper tel-

luride. This thin layer is *p*-type, degenerately conducting, and has a slight deviation from stoichiometry in the direction of copper deficiency. Almost any metallic grid makes low resistance contact to this *p*-type film, but an evaporated gold grid appears to give the best long term stability. This, except for encapsulation, completes the *p-n* heterojunction photovoltaic cell.

The method of fabricating the main CdTe base layer is shown in Figure 2. An approximately 18"

FIG. 2. — Vapor reaction apparatus for fabricating CdTe films.

long and 3" wide piece of molybdenum foil, previously cleaned by the steps of degreasing, nitric acid oxidation, and hydrochloric acid removal of the oxide, is placed cylindrically inside the upright bell of the quartz coating chamber. A cover plate of quartz or molybdenum rests a half inch above the bell. The coating chamber is heated externally such that the substrate temperature lies between 530 and 550 °C. A continuously operating mechanical pump maintains a low chamber pressure of 10-20 microns. Pre-dried and dispersed powder mixtures of Cd plus CdI₂ and of Te are fed gradually into regions B and A respectively, from suitably controlled dispensers above the O-ring seals. Frequently, finely divided silica or silicon carbide is also dispersed with the powders to achieve good feed control. The vapors of Cd, CdI₂, and Te originate from B and A and diffuse into the coating bell (as well as elsewhere) to react at all hot surfaces. The film one is concerned with is that which grows on the inside surface of the Mo foil. A 10 micron film of I-doped CdTe is formed in about 30 minutes. To achieve the desired high resistivity layer near the surface, which is depicted in Figure 1, one of the volatile column I or column V elements or its salts is added to the Cd + CdI₂ feed mixture during the last few minutes of the coating run. This acceptor-type impurity counter dopes or compensates the

last micron or two of the *n*-type base layer. CuCl or Sb metal have been found to be most satisfactory. The underlying *n*-type CdS film which is deposited at the very beginning, is grown by introducing H₂S gas at a pressure of 600 microns into region A rather than Te powder. The regular mix of Cd + CdI₂ is dispensed in region B. A small pool of gallium or indium is also introduced at region B to insure obtaining very low resistivity. If CdCl₂ or CdBr₂ is used in place of CdI₂, the gallium or indium is unnecessary.

A very schematic diagram of what is believed to be the electronic energy band profile of the Cu_{2-x}Te-CdTe heterojunction under short circuit operation is shown in Figure 3. The band gap of

FIG. 3.
The photovoltaic Cu_{2-x}Te-CdTe heterojunction.

copper telluride is smaller than that of cadmium telluride. Sorokin, Papshev, and Oush [1] recently found a value of 1.04 eV. The copper telluride is believed to be an indirect transition compound [2], with low absorption in the near infrared. However, the absorption coefficient in the blue and near ultraviolet is sufficiently high so that film thickness must be kept low. Cu_{2-x}Te is not very photosensitive, hence one wants the production of pairs to occur in the cadmium telluride. The cuprous telluride should only be as thick as necessary to avoid sheet resistance losses of a finished cell and insure reasonable temporal stability. Typical sheet resistance is 200 ohms/square. The resistivity of the CdTe base layer runs from 100 to 10,000 ohm-cm. The resistivity of the counterdoped or tailored region has not been determined. The acceptor states introduced by the copper or the antimony counterdoping are shown in the figure, also the shallow

donor states introduced by iodine and gallium (or indium). As is typified, the junction depletion region width in the CdTe is desired to be comparable to the optical absorption depth.

Typical spectral response of short circuit current is shown in Figure 4 for two different small area cells. To effect a small improvement in conversion efficiency an unsuccessful attempt has been made to obtain, via varying the counter dopants, an extrinsic response beyond the band edge cutoff. (An extrinsic response is seen in strength with CdS cells.) The differences in spectral response for the intrinsic effect, shown for the two cells of Figure 4, are related

FIG. 4. — The photovoltaic spectral response of two thin films cells at short circuit for equal energy input.

to depletion layer width, junction profile, etc..., rather than to impurity identity.

The V-I characteristic of one of the best small area cells is shown in Figure 5. The fill factor is high, and the total area efficiency under solar simu-

FIG. 5. — Load characteristic of a good small area thin film cell.

lation is 6 %. The gridding used in this case was an electroformed Ni mesh held in mechanical contact with a transparent adhesive.

The load characteristic for a good area large cell, 52.5 cm², is displayed in Figure 6. This characteristic was taken in direct sunlight at Wright Patterson Air Force Base in Ohio. The gridding in this case was vapor deposited gold and the cell was encapsulated with a layer of Krylon, an acrylic plastic. The efficiency is 5 %, with a maximum power output of nearly a quarter of a watt.

FIG. 6. — Load characteristic of a good large area thin film cell.

Krylon-coated cells have exhibited reasonable stability. Acrylic plastics are good moisture barriers, but they probably will not be useful for space applications since their transmission degrades under continued ultraviolet irradiation. Moisture is believed to be responsible for shelf degradation, but the mechanism is not yet understood. With Krylon coating, the best results obtained over a period of two years are that the short circuit current decays by 5 % per year and the efficiency about 2 1/2 % per year. At elevated temperature, depreciation takes place more readily. The behavior of short circuit current, open circuit voltage, and maximum power for in-air storage at 65 °C is shown in Figure 7. Although the maximum power changed rather little, the cell has undergone definite change, particularly an increase in open circuit voltage. Two things are important, here. One, it is unlikely that cells would see this high a temperature during on-earth storage periods and, two, it is not yet clear how much of the depreciation is due to water vapor and how much is intrinsic. Water vapor will not be encountered in outer space. What has been presented in Figures 6 and 7 is representative of the best results. Needless to say, there are cells which can degrade more rapidly than shown.

Inorganic transparent coatings have also been

FIG. 7. — Effect of storage at 65 °C on open circuit voltage, short circuit current, and maximum power of thin film cells.

examined for cell encapsulation. Al_2O_3 films of $\sim 1500 \text{ \AA}$ thick so far have given the best results. These thin coatings are applied in vacuo, in one or two minutes time, by electron beam evaporation of sapphire. It is usually necessary to cool the samples during deposition to avoid excessive radiation heating. However, the moisture resistance appears to improve with deposition temperature as is shown in the accelerated life test of short circuit current at 60 °C and 100 % relative humidity (see fig. 8). These tests of Al_2O_3 coated cells in air and in vacuum are continuing.

FIG. 8. — Effect of storage at 60 °C and 100 % relative humidity on short circuit. Current density of "first blue" Al_2O_3 -coated thin film cells.

Small area Krylon-coated cells can apparently withstand the thermal shock of being immersed from room temperature directly into liquid nitrogen. However upon slow cycling back and forth, the Krylon coating breaks away. Recently a silicone coating of a better thermal match than Krylon has been used successfully to obtain encouraging results

on thermal cycling, despite the fact that such a coating is probably insufficiently moisture impervious for good on-earth storage or appreciably resistant to outer space ultraviolet discoloration. A four cell submodule, with each 1 cm by 4 cm cell shingled to its neighbor with a lacy interconnection of conducting epoxy, has been cycled slowly between -130° and $+88^\circ \text{C}$ for more than 60 times without showing significant change in operating characteristics. The submodule efficiency was 4 %.

The following radiation resistance studies have been performed. Small area cells were exposed to Cobalt 60 gamma radiation, 5 MeV electron radiation, and 2.4 MeV proton bombardment. A dose of $1.6 \times 10^{17} \text{ R}$ of the gamma radiation and a dose of 2×10^{14} per cm^2 of the high energy electrons produced no effect on cell characteristics. R. L. Statler of the U. S. Naval Research Laboratory has conducted the proton tests and found that a 15 % decrease in short circuit current occurred at a total dose of 3×10^{13} per cm^2 . When compared to commercial single crystal silicon cells, these data are all encouraging but obviously much more study of radiation resistance is in order. Experiments with 1.5 MeV electron bombardment are in progress as well as studies of spectral response before and after bombardment. With the help of single crystals one hopes to understand both the earlier mentioned thermal as well as the radiation damage to heterojunction cells. Doses as high as 5×10^{16} electrons per cm^2 are being employed. The thermal damage degrades the blue response more than the red, the high dosage electron radiation does the reverse.

Let us now turn briefly to the single crystal studies. These have to do with approximately 1 cm^2 cells made from zone-refined *n*-type material or indium-doped material. The heterojunction is made from solution in the same manner as for the polycrystalline films (see fig. 9), but intentionally

FIG. 9. — Cross section of a Cu_{2-x}Te -CdTe single crystal solar cell crystal.

there is no counterdoping performed, since one wants to know depletion layer width accurately. Ohmic contact to the base layer is made with indium solder. The gridding for the cuprous telluride is nickel mesh with transparent adhesive.

The room temperature efficiency of these cells is generally higher than for the thin film cells as a result of higher open circuit voltage. Figure 10

FIG. 10. — Effect of orientation on the load characteristics of single crystal solar cells (orientation and fill factors shown).

exhibits some careful work on $V-I$ characteristics of cells made from a given crystal boule but using slices having different crystallographic orientations. Note the dependence of the open circuit voltage on crystal orientation, the higher values for junctions made parallel to planes of greater atomic density.

FIG. 11. — Effect of base resistivity on the load characteristics of single crystal solar cells (shallow donor concentration shown).

All these were good cells as indicated by the high fill factors.

Figure 11 illustrates the variation of $V-I$ characteristics with concentration of shallow donors in the base material. As one progresses from a concentration of several times 10^{14} to 2×10^{17} per cm^3 , the depletion layer width changes from several microns to less than a tenth of a micron. Bulk series resistance degrades the $V-I$ characteristic for lightly doped cells, but it is clear nonetheless that highly doped material with its consequently narrow junction width leads to poor results. For the highly-doped cells, Figure 12 on spectral response

FIG. 12. — Effect of base resistivity on the spectral response of single crystal solar cells (shallow donor concentration shown).

indicates an increasingly poor collection efficiency with increasing wavelength. Carriers are produced beyond the depletion region and this is interpreted to mean that minority carrier lifetime in the absence of an electric field is low [3]. One could conclude from Figures 11 and 12 that the counterdoped region in the thin film cells should be adjusted to give a net donor density of a few times 10^{15} per cm^2 .

Figure 13 gives a good indication of the diffusion (or built-in) voltage available in the $\text{Cu}_{2-x}\text{Te}-\text{CdTe}$ junctions. A number of single crystal cells were illuminated by a short pulse of variable light intensity from a G. E. FT-503 flash tube. The pulse was less than $50 \mu\text{s}$ in duration. Although transient heating of the junction region during the most intense pulses cannot be ruled out, it does appear that the built-in voltage at room temperature is nearly 0.9 volts. At liquid nitrogen temperature, the value becomes 1.05 volts, almost the same increase observed as for the band gap of CdTe. The values at both temperatures are about 3/5 the CdTe gap. However, the open circuit voltage at 77 °K under a one sun intensity is a considerably greater fraction of the built-in voltage than is the case at room temperature. It is hoped that a

FIG. 13. — Dependence of open circuit voltage on light intensity (pulsed) for single crystal solar cells.

junction profile can be found, with suitable doping, that will reduce the forward current at room temperature and allow a greater one-sun open circuit voltage, hence greater efficiency. Good single crystal cells have exhibited 8 % conversion efficiency between 77 and 130 °K. Were appropriate antireflection coatings used for such cells, the efficiency would lie between 9 and 10 %. These figures could conceivably be the goals for thin film cells.

In summary, this paper is a very brief report on the present status of $\text{Cu}_{2-x}\text{Te-CdTe}$ photovoltaic

cells for future space power applications. The method of fabrication and some of the operating characteristics have been described, also some of the supporting studies on single crystals. It appears the most pressing problem lies in achieving stable performance of thin film cells at elevated temperatures. It is our belief, however, that this type of cell is one of most promising of today's thin film types, and continued investigations to further its development are under way.

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