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DEVELOPMENT OF COPPER SULFIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

Eighth Technical Progress Report for the Period April 1—June 30, 1981

By
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Westinghouse R & D Center
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J. R. Szedon, W. J. Biter, and H. C. Dickey

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1. SUMMARY

The most important accomplishments during this period were to demonstrate and to elucidate further the complex effects that occur during the aging of $\text{Cu}_2\text{S}/\text{CdS}$ thin-film solar cells in flowing wet oxygen. There are two distinct effects. At constant illumination, the short-circuit current of cells aged at room temperature consistently decreases with time. The second effect, related to diode opposing current, is more involved and may result from several competing mechanisms. Over the short term (~ 4 to 5 hours), the magnitude of diode opposing current decreases; thus, at constant J_{SC} , the open-circuit voltage of cells is higher than before aging. After ~ 20 hours of aging, opposing current generally returns to the level achieved after hydrogen annealing which immediately preceded the aging sequence. At constant J_{SC} , the values of V_{OC} are comparable to those obtained before aging. Of course, since J_{SC} at constant illumination is reduced considerably during aging, the cell performance is much lower.

Optical measurements of the spectral transmission of the Cu_2S layers in a cell content have been made using a silicon detector epoxied to the back of a CdS cell after the copper foil substrate was removed. This new approach allows detection of small changes in low-level signals and hence is suited to determining if changes in the optical properties of Cu_2S layers are responsible for J_{SC} degradation during aging.

From our measurements, there is no significant change in Cu_2S transmission behavior for wavelengths ranging from 525 to 1000 nm during wet-oxygen aging for periods of 2 to 36 hours. This leads us to conclude that the decrease in J_{SC} at constant illumination, for the aging experiments in a flowing wet-oxygen ambient, arises because of changes in minority-carrier transport properties of the Cu_2S . Among the

possibilities are changes in the minority-carrier diffusion length within the Cu_2S , in the free-surface recombination velocity, or in the recombination velocity at the heterojunction.

Before developing a method for using an epoxied silicon detector to measure optical behavior of the Cu_2S layer, we explored the possibility of using a junction-containing wafer of silicon as a substrate for deposited CdS films. Some monolithic structures were successfully fabricated. Comparisons were made of CdS grain structure details in the junction detector area and in an adjacent metallized area. The latter is important to allow fabrication of a state-of-the-art CdS cell, the performance behavior of which may be correlated with the Cu_2S optical characteristics measured by the detector. We concluded that too great a difference existed between the two regions as regards Cu_2S topology and grain boundary details. No further effort was applied since the use of an epoxied detector after cell fabrication was simpler and free of ambiguous influences.

2. INTRODUCTION

2.1 Objective and Tasks

The objective of this program is to develop and document cell-processing methods for 9% efficient $\text{Cu}_2\text{S}/\text{CdS}$ thin-film solar cells and to assess selected alternate routes for achieving cells with 10% or higher efficiency. There are three specific tasks for the current phase of the program: (1) to improve baseline processing methods to provide greater control over the reproducibility of cell performance; (2) to investigate means for making more stable, high-efficiency solar cells; and (3) to evaluate alternative methods of forming the grid electrodes which reduce the high cost of the thick evaporated gold grids presently being used.

Tasks 1 and 3 had been completed earlier in the program. During the preceding period our efforts were concentrated on Task 2. Work during the period covered by this report has been directed to a more comprehensive treatment of several remaining issues on Task 2.

2.2 Technical Approach

2.2.1 Review

In our efforts to date for dealing with the issue of stability in $\text{Cu}_2\text{S}/\text{CdS}$ thin-film cells, we have characterized changes in photovoltaic performance during the course of aging completed cells in various gaseous ambients. The novel aspect of the work was to conduct a complex, extensive series of tests using a quartz stress/evaluation (S/E) tube. In this tube the cells could be first annealed in H_2 at elevated temperature to produce high PV performance, then subjected to flowing gas ambients of controlled composition without intermediate

atmospheric exposure, and finally evaluated in terms of PV performance, as required. Even with this capability, we found that one-time reductions in J_{SC} occurred when the S/E tube ambient was changed from that used for hydrogen annealing to inert, flowing N_2 or Ar.* Moreover, in wet oxygen at room temperature, significant reductions in J_{SC} occurred with time constants as low as one hour. This suggests that cell-performance results during aging which have been reported in the literature may reflect influences of short exposures to uncontrolled ambient conditions.

A wide variety of mechanisms has been suggested as being important in controlling short-circuit current in Cu_2S/CdS thin-film cells. Rothwarf and Windawi have compiled the following list⁽²⁾:

- (a) Changes in crystallographic phase from chalcocite (with high optical-absorption coefficient) to a chalcocite-djurleite mixture of lower copper content and lower optical absorption.⁽³⁾
- (b) Changes in minority-carrier diffusion length in the Cu_2S layer due either to mobility or lifetime changes.⁽⁴⁾
- (c) Changes in surface recombination velocity related to the presence of surface oxide in the Cu_2S .⁽⁵⁾
- (d) Changes in the heterojunction barrier related to oxygen at the interface.⁽⁶⁾
- (e) Changes in junction profile due to phases with different band gaps.⁽⁷⁾

*Ref. 1, pp. 26-32.

- (f) Changes in carrier transport through a dislocation array postulated to form within the Cu_xS as structural and stoichiometric changes occur due to oxidation.⁽⁸⁾
- (g) Electromigration of copper ions in the vicinity of the heterojunction.⁽⁹⁾
- (h) Band bending in the Cu_xS layer as its stoichiometry changes.⁽¹⁰⁾
- (i) Changes in optical absorption due to changes in the degeneracy of the Cu_xS layer.⁽²⁾

Only in the cases of carrier transport through a dislocation array⁽⁸⁾ and the degeneracy control of free carrier absorption⁽²⁾ have numerical estimates been made of the expected influence on short-circuit current behavior. In both of these cases, no direct evidence of the existence of the proposed mechanisms has been obtained in experiments correlating the electrical effects with the physical ones.

Change in the absorption characteristics of the Cu_xS layer is the most frequently invoked mechanism to account for the short-circuit current decrease in aged $\text{Cu}_2\text{S}/\text{CdS}$ cells. For that reason, we have explored at length methods for obtaining direct measurements of the optical properties in Cu_2S films used in thin-film cells. We have successfully formed $\text{CdS}/\text{Cu}_2\text{S}$ photodetectors at the back surfaces of CdS films before and after completion of the normal front-surface solar cell.* Detectors formed after cell fabrication have been invariably coupled electrically to the front-surface junction. This has precluded their use in measurements of the optical properties of the front Cu_2S layer. During this period, we have explored the use of a silicon photodetector at the back of the CdS layer. In addition, we have carried out a series

*Ref. 1, pp. 36-43.

of electrical characterizations of variously aged cells in terms of their J_{SC} versus V_{OC} behavior using several levels of illumination. This approach is useful for quickly detecting changes in junction current-controlling mechanisms. We have previously applied it to differentiate influences of cell fabrication details, such as length of immersion in CuCl solutions during barrier formation, on cell behavior.*

2.2.2 Cu_2S Optical Measurements Using Silicon Detectors

Our previous work on this program has shown that it is possible to make photoresponsive CdS/ Cu_2S junctions at the back surface of a CdS film which is used also for a conventional thin-film solar cell.† Some processing refinements would be required to eliminate the electrical coupling, assumed to be due to through-the-film defects, between the front and back Cu_2S layers. This coupling currently precludes using these detectors to measure light transmitted through the front-surface Cu_2S layer. Implementing the refinements was not undertaken since there is a strong possibility that aging effects in the back-surface detector would hamper its value in studying aging effects on the optical properties of front-surface layers of Cu_2S .

In order to get a back-surface detector, the response of which would be stable under the conditions of the aging experiments, we decided to use a silicon p-n junction. Initially, we considered using specially prepared silicon wafers with diffused junctions as the substrate for CdS deposition. Ultimately, we hoped to produce the structure shown in Figure 1. Such a structure would permit characterization of optical transmission properties of the Cu_2S region (at the right of the specimen). The p-n junction response for light impinging on the region of CdS from which the Cu_2S was removed would serve as a reference in various measurements.

*Ref. 11, pp. 124-127.

†Ref. 1, pp. 40-42.

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Figure 1. Diagram of a monolithic structure for measuring the transmission of light through a Cu₂S layer by using a photosensitive junction in a silicon wafer.

This approach has a number of desirable features. The silicon detector should be very sensitive, uniform in its local response, and stable in its characteristics under the conditions anticipated for its use. In addition, the high refractive index of silicon should promote good optical coupling into the detector of light entering the CdS film. Several potential disadvantages for this approach were identified before any work was done. First, the structure of CdS films deposited on a silicon substrate may differ substantially from those used for actual cells. This could raise questions about experimental effects which might be influenced by the CdS grain structure. To resolve this issue might require considerable experimental effort. Another disadvantage is that the preparation of silicon substrates having diffused, photosensitive junctions with accessible contact regions is complex and time consuming.

During the course of studies on using silicon substrates for CdS deposition to meet the requirements described above, a simpler approach using a silicon detector was tried. The basic idea of this method is shown in Figure 2. First, a completed $\text{Cu}_2\text{S}/\text{CdS}$ cell is mounted with a wax-to-glass support slide (Figure 2a). The copper foil substrate is removed, preferably by peeling from the CdS film, and the exposed CdS surface is then attached to a silicon photodetector using transparent epoxy. After the wax-to-glass support slide is removed, a small area of the Cu_2S film is etched away to provide a reference area for optical measurements (Figure 2b). With regard to reflection of incident light, the reference CdS area and the Cu_2S area should be very similar. Since the refractive indices of CdS and Cu_2S are nearly the same (3 versus 3.5, respectively) and since the topology of the etched CdS surface should replicate that of the original outer Cu_2S surface, the intensity of light transmitted through the reference area to the underlying Si detector should be equal to that transmitted into the Cu_2S layer.

The use of an epoxied silicon photodetector for optical characterizations of the Cu_2S layer in a cell structure has several advantages. First, there is a minimum of physical disturbance to Cu_2S

Figure 2. Top: Mounting of a completed $\text{Cu}_2\text{S}/\text{CdS}$ cell to a temporary superstrate to permit removal of the copper foil.

Bottom: Final device configuration after the thin-film cell is epoxied to a silicon photodetector.

layers previously formed by standard cell processing. Second, high-quality silicon detectors can be used. Third, good reproducibility, even of low-level signal results, should be possible since the test specimen and the detector are functionally monolithic. One minor matter of concern is that the aging conditions for thin-film cell investigations be compatible with the use of the epoxy adhesive.

2.2.3 Characterization of Junction Transport

In addition to the conventional characterization of $\text{Cu}_2\text{S}/\text{CdS}$ cells in terms of dark and illuminated I-V behavior, we have used another technique which is more useful in revealing details of current transport, particularly changes due to processing or aging. This involves plotting V_{OC} versus $\log I_{\text{photo}}$ over a range of light intensities (~ 50 to 1000 mW/cm^2) by varying the distance between the simulator and the cell under test. This method has an advantage in that it eliminates series resistance contributions which might be significant in dark I-V characterizations at high current levels. Furthermore, as pointed out by Panayotatos and Card,⁽¹²⁾ it is valid for determining n -values controlled by details of recombination or trapping which occur under actual illumination conditions. The determination of n -values from dark I-V characteristics may be inappropriate in this regard. Haines and Bube have used this approach in studying the role of a deep donor level in $\text{Cu}_2\text{S}/\text{CdS}$ cells which can act as a recombination level reducing J_{SC} or as a tunneling center reducing V_{OC} .⁽¹³⁾ At Westinghouse the technique has been applied to $\text{Cu}_2\text{S}/\text{CdS}$ thin-film cells to assess the influence of processing details, such as duration of the CuCl immersion step in barrier formation, on current transport within cells.* In the present case with aged cells, if the heterojunction transport properties were affected we would expect to see changes in values of n -factor or in pre-exponential coefficients for the curves of V_{OC} versus $\ln I_{\text{SC}}$.

*Ref. 11, pp. 124-128.

In order to relate measured values of J_{SC} with illumination intensity, we used an auxiliary silicon cell mounted adjacent to the stress/evaluation (S/E) tube in which the thin-film cells were maintained. During the course of the pre-aging and aging experiment, the photocurrent of the auxiliary cell was set to three specific levels by adjusting the simulator-to-cell distance. As a second check on the illumination intensity, the silicon reference cell mounted within the S/E tube was also characterized during the aging experiment.

3. JUNCTION TRANSPORT CHARACTERIZATION OF AGED $\text{Cu}_2\text{S}/\text{CdS}$ CELLS

3.1 Background

Four cells were used for studies of detailed $\ln J_{\text{SC}}$ versus V_{OC} behavior, as influenced by aging in wet O_2 at room temperature. The cells were from two CdS films and had been fabricated at the same time. The thickness of the gold grid electrode was only 1.8 μm , rather than the 2.5 μm which is conventionally used in our cells. The cells were subjected to a long period (~ 290 hours) of hydrogen annealing at 150°C , primarily to ascertain that a condition of maximum efficiency had been achieved.

After their installation in the S/E tube, the cells were subjected to ~ 150 hours of aging in wet argon; ~ 300 hours in wet nitrogen; and 5 hours in wet oxygen. Short anneals in H_2 at 150°C were given between the aging intervals. No significant trends in degradation of PV parameters were noted during the aging intervals in wet AR or N_2 , as discussed in reference 1. Prior to the experiment of present interest, the cells were annealed in H_2 at 150°C for a period of about 270 hours. Several times during the course of this anneal, in-situ measurements were made. This was done in an attempt to restore the performance of the cells to the levels measured after the short H_2 anneals which followed the wet O_2 aging conditions. Recovery of short-circuit current capability ranged from 88 to 96% of the goals.

3.2 Behavior Initially and After Short Aging Interval in Wet O_2

One of the experimental cells developed erratic contact symptoms early in the test. The other three were measured, along with the silicon reference cell inside the S/E tube, prior to aging. The lamp-to-cell distance was varied to produce illumination levels of about 16,

43, and 90 mW/cm² as indicated by the silicon reference cell.

Corresponding readings on a second monitor cell outside the S/E tube were noted and used in setting the simulator-cell distance on subsequent occasions. Cell performance was characterized under computer-control, and the results were processed and stored for subsequent analysis.

The three curves in Figure 3 show some spread in behavior of the cells prior to aging. After aging in wet oxygen for 4.5 hours, the cells exhibited smaller differences in behavior as shown by the data in Figure 4. All cells responded with lower values of J_{SC} than were obtained in the pre-aging case for each of the three levels of illumination used for the evaluation. At fixed J_{SC} , from the curves fitted to the data of Figure 4, all three cells had higher values of open-circuit voltage than before aging.

3.3 Results of A Longer Aging Interval

After additional aging for 21.5 hours in wet oxygen, all three cells exhibited further decreases in J_{SC} for the illumination levels used in testing. For two of the cells, the $\ln J_{SC}$ versus V_{OC} behavior had very nearly the same slope and intercept for J_0 as the behavior prior to aging. Figure 5a shows this for one of the cells in question. In the case of the third cell, the slope was somewhat higher than initially and at constant J_{SC} (not illumination) this cell had still higher values of V_{OC} than it did originally (see Figure 5b).

3.4 Discussion

From these results we conclude that aging in wet O₂ can have a complex effect on Cu₂S/CdS solar cells. Although J_{SC} at constant illumination is consistently reduced during aging, during early stages diode opposing current is reduced, allowing achievement of higher open-circuit voltage values at fixed values of J_{SC} . With further aging, opposing current increases. We doubt that the behavior observed in two of the cells -- a return to virtually the same opposing current behavior

Figure 3. Photovoltaic behavior of cells in S/E tube after in-situ anneal prior to aging in wet O_2 . Straight lines are fit by linear regression to the data.

Figure 4. Behavior of cells after 4.5-hour aging in wet O_2 , with straight lines being fit by linear regression to the data.

Figure 5. Effects of aging in wet O_2 for 21.5 hours on the photovoltaic performance of two cells.

as before aging -- is fortuitous. On the basis of those results, we are led to conclude that the main effect of long-term aging in wet O_2 is to reduce J_{SC} . This reduction may be due to changes in the generation rate of photocarriers, e.g., resulting from lower absorption in the Cu_2S , or to changes in the collected fraction of photocarriers due to recombination losses at the outer surface or within the Cu_2S layer. As discussed in Section 2.2.2, spectral measurements of the absorption of the Cu_2S films in a cell context would help to clarify this issue.

4. OPTICAL MEASUREMENTS OF Cu_2S PROPERTIES IN A CELL CONTEXT

4.1 Monolithic Structures Using Silicon Substrates

A discussion of the advantage and potential problems associated with fabricating and evaluating $\text{Cu}_2\text{S}/\text{CdS}$ cells formed on a silicon substrate is given in Section 2.2.2. A pn-junction detector formed in the silicon substrate could be very useful in characterizing the spectral transmission behavior of a thin-film cell prepared on its surface. Our initial concern was that the polycrystalline structure of CdS films deposited on a silicon substrate would be significantly different from that in state-of-the-art cells prepared on zinc-plated copper foil substrates. To define the scope of problems in this regard, we prepared some physical specimens, depositing a CdS film on silicon wafers.

For the study of structural details, part of the wafer area was bare silicon and part had a complex layered-metal structure. First, layers of titanium, palladium, and silver were sequentially evaporated (to thicknesses of 480, 200, and 2000Å, respectively) onto the silicon. This arrangement is used to provide ohmic contact to the top diffusion in some np-junction solar cells using silicon. Subsequently, we plated copper, then zinc, on the silver surface to provide for a back ohmic contact to the deposited CdS layer. This multi-layer metal arrangement would be required for that part of a test structure in which a working $\text{Cu}_2\text{S}/\text{CdS}$ cell would be needed. The bare part of the silicon surface, of course, would accommodate that part of a test structure used for optical characterization of the Cu_2S layer by an np-junction in the silicon.

We used the technique of Cu_2S formation and removal to delineate the grain boundary structure on the top and side surfaces of the CdS films of interest. The side surfaces were those produced by fracturing

the specimens. This method was developed earlier in the current program.* The results were not encouraging for our intended application.

The CdS film deposited over the metallized portion of the silicon substrate had a definite columnar structure throughout the upper two-thirds of its thickness, as shown in Figure 6a. For the region within $\sim 3 \mu\text{m}$ of the metal surface, small randomly oriented grains are present. Only those grains with the most favored orientations for growth persist above about $13 \mu\text{m}$ in the film, giving grains with top-surface diameters of several micrometers. State-of-the-art CdS films on Zn-plated copper foil exhibit grains which are more like inverted cones, with top-surface grain diameters comparable to those shown in Figure 6a.†

For the CdS film grown on the bare silicon substrate, the structural details were much different from those in the metallized area, as shown in Figure 6b. Particularly near the free top surface of the CdS film, the complexity of the grain structure is much greater than for the film grown on metal. We believe it would be difficult to correlate the optical properties of Cu_2S layers formed on a CdS film, such as that shown in Figure 6b, with the behavior of $\text{Cu}_2\text{S}/\text{CdS}$ cells formed on a metallized silicon surface.

Concurrently with these experiments, work was being done on epoxying Si detectors to the back surface of $\text{Cu}_2\text{S}/\text{CdS}$ cells from which the copper foil was peeled away. This allowed preparation of test structures as shown earlier in Figure 2. In obtaining successful results with the epoxied detector as described in the next section, we elected not to pursue further the monolithic approach with its potential grain structure problems.

*Ref. 14, pp. 27-34.

†See Fig. 11 in reference 14 for details of the grain structure in state-of-the-art films, as revealed by the same methods of specimen preparation.

(a)

Small white scale marker: 5 μm

(b)

Figure 6. Comparisons of grain structure (revealed by SEM examination after Cu_2S formation and removal) within $\sim 40\text{-}\mu\text{m}$ -thick CdS films evaporated on bare (a) and metallized (b) portions of a polished silicon substrate.

4.2 Results Using an Epoxied Silicon Detector

With a silicon solar cell epoxied to the back of a $\text{Cu}_2\text{S}/\text{CdS}$ solar cell (from which the copper foil had been peeled), as discussed in Section 2.2.2, it became feasible to characterize the spectral transmission of Cu_2S layers fabricated for solar cell applications. We arranged for the output light beam from a computer-controlled monochromator to fall on a galvanometer-driven mirror. The mirror position was also controlled by the computer (Digital Equipment Corp. MINC). For each wavelength used by the computer program, the light-beam was deflected by the mirror to fall on two different areas of the specimen. One area of the cell from which the Cu_2S had been etched provided a measure of the light transmitted through the CdS film, as detected by the silicon solar cell. For the other area, the light passed through the Cu_2S film. Figure 7 gives the response of the Si detector for each of these regions. Since the values of the refractive index for Cu_2S and for CdS are very similar and since there were no major differences in the surface morphology of the two illuminated areas, the intensity of the light beam entering each of the test areas should be nearly the same. Thus, at each wavelength, the ratio of the detector response for the Cu_2S region to that of the CdS region gives the relative transmission for the Cu_2S film. Figure 8 is an example of such a relative transmission characteristic for a specimen immediately after the specimen preparation step, which followed a short anneal in pure H_2 to give good J_{SC} response. Two curves (solid and dashed) are shown as examples of the reproducibility of this measurement method.

After aging in flowing wet oxygen at room temperature for two hours, there was no detectable effect for wavelengths below 950 nm. In the range 950 to 1800 nm, there was a slight decrease in the rate of detector response. Additional aging, for a total of 36 hours in flowing wet oxygen did not produce any further detectable change in the measurement results, which are shown in Figure 9.

Figure 7. Spectral transmission results before aging, in terms of uncorrected detector response, for the CdS alone and for the Cu₂S/CdS combination using the special measurement structure of Fig. 2.

Figure 8. Ratio of detector response (from Fig. 7) for light transmitted through unaged Cu_2S and CdS layers to response for transmission through CdS alone.

Figure 9. Silicon detector response ratio after aging of the $\text{Cu}_2\text{S}/\text{CdS}$ specimen for 36 hours in wet oxygen.

From the results of these measurements, we conclude that the optical properties of thin Cu_2S layers used in our state-of-the-art solar cells are not changed significantly in the wavelength range of ~ 525 to ~ 1000 nm by the wet-oxygen aging conditions which result in large decreases in the J_{SC} performance of such cells. Thus, it seems to us that the degradation in the J_{SC} behavior of these cells due to the combined action of moisture and oxygen must be caused by changes in the electronic properties of cell, rather than being due to changes in optical absorption of the Cu_2S layer.

5. FUTURE PLANS

We expect to evaluate in more detail the changes in J_{SC} versus V_{OC} behavior of Cu_2S/CdS cells aged in flowing wet O_2 . Particular emphasis will be placed on the relationship between the pre-exponential current factor and the diode ideality factor.

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