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

Tenth Technical Progress Report for the Period October 1—December 31, 1981

By
J. R. Szedon

April 23, 1982

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Westinghouse R&D Center
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Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

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J. R. Szedon
Westinghouse R&D Center
Pittsburgh, PA 15235

ABSTRACT

During this period three new stress/evaluation tubes have been assembled for use in aging and testing Cu_2S/CdS cells in a controlled, flowing gas ambient. One of the tubes can be accommodated in a controlled humidity cabinet, which will allow acquisition of information on the temperature and humidity acceleration of degradation involving short-circuit current and diode opposing current in Cu_2S/CdS cells. Evidence has been found which supports a structural origin for the deep-donor tunneling states which can control opposing current in these cells. An improved gas-handling system has been assembled to provide a high-humidity environment for aging cells at room temperature.

1. SUMMARY

During this period a new phase of work on the program has begun to characterize and improve the stability of Cu_2S/CdS thin-film solar cells. Three tasks are being undertaken in this regard. They are: 1) identify major mechanisms causing performance degradation in cells, 2) improve the stability of cells by encapsulation, 3) improve the intrinsic stability of cells by modifying the material properties and/or cell structure.

The new stress/evaluation tubes have been fabricated to permit maintaining cells in a controlled, flowing gas ambient during annealing, aging, and testing without any intervening exposure to the laboratory environment. One of the tubes is shorter than the others to permit its use within a controlled humidity chamber. Cells aged and tested in that tube should provide information on the independent acceleration factors for cell degradation which are associated with humidity and temperature. Each tube can accommodate ten cells.

A better arrangement has been devised for controlling the ambient atmosphere within the S/E tube. Four separate input gas lines are provided, two of which have micrometer-adjustable valves. The other two lines, each separately valved, permit flushing the S/E tube with house nitrogen to expel air and oxygen before and after hydrogen is introduced for in-situ annealing. During use of nitrogen or hydrogen the exhaust from the S/E tube bubbles through an oil column. For aging and testing of cells in a wet oxygen ambient, the nitrogen and hydrogen lines and the oil bubbler are valved off. Two streams of oxygen are supplied through the micrometer valves, one of which controls the flow through a water bubbler. The humidified and dry oxygen streams are mixed in a chamber containing a hygrometer. The output of this chamber,

at the desired humidity, is fed to the input of the S/E tube. Exhaust gas from the S/E tube bubbles through water to provide a sealed system with flowing oxygen of controlled humidity.

In planning the technical approach to improve cell stability, we have chosen two degradation effects which occur during the storage of unprotected Cu_2S/CdS solar cells. One is the progressive loss of short-circuit current capability during aging in a wet oxygen ambient; the other is the change in diode opposing current, which appears to be due to modulation of electron tunneling that occurs via deep donor states in the Cu_2S. The first presents, in principle, no problems as regards characterization. Preliminary results show the degradation to be a sum of two exponentials. Thus, differentiating between the two time constants and determining their sensitivity to temperature and to moisture content should be straightforward. For the opposing current, on the other hand, information is limited and complex. In one of three devices studied earlier, the effective density of ionized donors (which modulates the tunneling barrier) in the Cu_2S space charge region decreased over a 22-hour period. For the other two devices, an initial decrease in ionized donor density was followed by a return to near pre-aging values.

We have yet to obtain empirical evidence of the regular behavior of a parameter relevant to the tunneling model. However, we have re-analyzed some data obtained earlier which fit the tunneling model. In that case, the effective density of ionized donors progressively increased as the CuCℓ immersion time during barrier formation was increased from 5 to 140 sec. We think these results imply that the density of tunneling states increases with the thickness of the Cu_2S layer, suggesting that the states are structure-related. If that is the case, reduction of the density of these centers may be possible by modifying the structure of the interface region. Ultimately, such modified structures may show greater stability during aging, as regards the degradation of opposing current behavior.

2. INTRODUCTION

2.1 Objective

The objective of this program is to characterize and improve the stability of Cu_2S/CdS thin-film solar cells having conversion efficiency values of 9% or greater. Specifically, the current phase of the program is concerned with identifying mechanisms which degrade cell performance, improving the stability of cells by encapsulation, and improving the intrinsic stability of the cells by modifying the cell structure during or after fabrication.

2.2 Background

The present contract has involved two phases preceding the current one which began with this quarter. During the first phase, the emphasis was on identifying and duplicating the critical steps in the fabrication of 9% efficient cells by the team at the Institute of Energy Conversion of the University of Delaware. Three areas requiring special attention were identified: minimizing the area of the Cu_2S/CdS heterojunction by controlling the CdS grain structure through accurate maintenance of substrate temperature, controlling the termination of the barrier formation chemistry step, and avoiding temperatures in excess of 100^oC for periods of 5 min or longer when surface-adsorbed moisture or oxygen could be present on the cells. Details are treated in Reference 1.

The achievement of the goals of the first phase led to work which addressed three issues during the second phase. These were: 1) improving cell processing methods to provide greater control of the reproducibility of cell performance, 2) investigating possibilities for more stable, high-efficiency cells, and 3) evaluating alternate methods of grid-electrode formation to replace the high cost of using thick, evaporated gold grids. Use of an argon gas knife to dry the cell surface after immersion in active solutions was shown to be a practical way of improving control during barrier processing. Replacement of the gold layer by a thick layer of lead deposited on thin layers of copper or of gold was demonstrated as producing a limited performance loss in cells, which might be acceptable on a cost-performance basis. Use of electrodeposited gold grids gave higher cell performance than did the baseline evaporated grid method.

As part of the task to produce high-efficiency cells, we recognized that departures from baseline processing methods or device fabrication approaches might affect the stability of cell performance. We decided that a preliminary characterization of the stability of baseline cells was desirable. Those efforts yielded interesting results.[2,3] We found that the short-circuit capability of unprotected cells can be lost at room temperature during exposure to a moist, oxygen ambient. Furthermore, there are changes in the open-circuit voltage behavior at constant J_{sc} of cells during such aging. These changes are consistent with modulation of the electron tunneling current which flows between the CdS conduction band and the Cu_2S via deep electron donors in the CdS space charge region.[4,5] Aging in dry oxygen or in wet argon or nitrogen does not produce these effects, at least during the first 100 to 400 hours.

Having defined a reproducible processing method for fabricating high-efficiency Cu_2S/CdS cells and having preliminarily identified several major degradation effects in these cells due to the combined effects of moisture and oxygen, we have embarked on the present phase of the program. Its focus is to improve the stability of cell performance by several means which are discussed below.

2.3 Approach

On the present phase of the program we will focus on issues involving the stability of Cu_2S/CdS thin-film solar cells. Our primary goal is to improve the stability of these cells. This will be done either by defining a suitably protective encapsulation method (which can be implemented at low cost) or by modifying the material properties and device structure to eliminate or suppress those mechanisms which cause degraded cell performance. In either case, we must first determine which device characteristics are the most appropriate indicators of degradation mechanisms. From our earlier work, the loss of short-circuit current capability and the changes in open-circuit voltage due to tunneling control of diode opposing current seem to be the most significant sources of cell degradation under storage conditions. The loss of open-circuit voltage capability due to copper shunt development under illuminated conditions is a matter identified and being pursued at other laboratories.[6]

The second aspect of our approach to the stability problem is to determine the kinetic behavior of the short-circuit current loss and of the tunneling mechanism which controls open-circuit voltage. We have some preliminary information on the former. At room temperature in a moist (80 to 100% RH) flowing oxygen ambient the short-circuit current loss gave evidence for two mechanisms; one with a time constant of 3 to 5 hrs, the other with one of 30 to 50 hrs. By examining a matrix involving other temperatures and levels of moisture content, we expect to define the kinetics of the short-circuit current degradation. It will be necessary to establish if a comparable kinetic characterization of the tunneling model can be made.

Part three of our approach is to determine whether encapsulation or modification of the cells can significantly reduce the rate at which photovoltaic performance degrades. The combination of water vapor and oxygen appears to be necessary for the degradation we have observed during storage of cells. By slowing the ingress of either species through an encapsulant, or by denying either species the opportunity to react with the cell materials, we should inhibit degradation of cell performance. While such protection could be afforded by hermetic packaging methods, the cost of doing so would not be acceptable. Our simple approach here is to determine if state-of-the-art methods of laminated encapsulation used for silicon solar cells have much value in protecting Cu_2S/CdS cells.

In order to rule out the possibility of reaction between the cell materials and the encapsulants, we plan to prepare specimens in which the length of the path from the edges of the package to the cell itself is varied. In this way the rate of cell degradation associated with moisture or oxygen ingress should reflect the effect of the path length.

As regards the reduction of short-circuit current capability in cells aged in wet oxygen, our present hypothesis is that changes in the surface recombination velocity of the Cu_2S layer control this behavior. There is also the possibility that minority carrier transport through the layer is reduced due to recombination at dislocation arrays as the stoichiometry of the Cu_2S changes during oxidation. In either case, the Bogus approach of applying a thin film of copper to the Cu_2S layer should minimize degradation effects. Bogus and Mattes have reported positive results for the appproach when cells were heated at 180°C in air.(8) We will be using thin films of Cu and ion implantation, probably of a nonreactive species, to determine if beneficial results are achieved regarding aging in wet oxygen.

We feel that this approach is important since it begins to address for the first time the stability issue in these cells from the point of view of fundamental mechanisms and of empirically meaningful stress and test conditions. The lack of a resolution earlier to the stability problem in these cells has hampered their acceptance as practical, albeit developmental, low-cost solar cells. It is important to correct this defect as soon as possible. Even with the present emphasis on studying the copper sulfide/cadmium sulfide thin-film cell, the understanding to be gained regarding related heterojunction cells, e.g., those incorporating $CuInSe_2$ as the base material, should be very valuable.

2.4 Program Tasks

The current phase of the program has three tasks:

Task 1. Identify major degradation mechanisms. This task will be addressed by subjecting cells to selected conditions of temperature and of moisture content of the gas ambient and characterizing the performance of the cells as a function of time. Periodically, cells in which significant performance changes are observed will be analyzed for physical and chemical changes to determine if any correlation exists with the electrical changes.

Task 2. Improve environmental stability by encapsulation. A baseline encapsulation method currently employed for silicon web solar cells will be used with Cu_2S/CdS thin-film cells. Attention will be given to determining if the encapsulant materials have a degrading effect on cell performance. If the encapsulation method is successful, an assessment will be made of the improvement as compared to the behavior of unprotected cells under severely degrading conditions determined in work on Task 1.

Task 3. Improve the intrinsic stability of Cu_2S/CdS cells. Modification of the Cu_2S layer will be attempted by deposition of a thin layer of Cu and by ion implantation. Evaluations will be made of both types of actions on the degradation in cell performance during aging. Comparisons will be made to determine if significantly more stable performance is achieved than in the baseline cells studied in Task 1.

3. PROGRESS

3.1 Construction of Stress/Evaluation Tubes

Since the degradation behavior of Cu_2S/CdS cells during storage is sensitive to the presence of oxygen and water in combination, it is important that a means exist for controlling the atmosphere to which the cell is exposed before and during the stress period and during cell evaluation. We have previously reported using a special stress/evaluation (S/E) tube for this purpose.* For the current work we fabricated three additional S/E tubes which allow us to carry out simultaneous aging experiments that can last for periods of weeks.

Figure 1A shows a completed S/E tube (top), together with its component parts. Figure 1B illustrates the arrangement of clips (d) and spring probes (c) used for contacting individual cells mounted on the substrate support block (a). The spring probes are screwed to an insulating piece of Micalex® (b) which is fastened to the support block. A hole through the length of the support block accepts a stainless steel tube (e). By this arrangement, the flowing gas ambient is introduced into the S/E tube. The tube (e) fits through one of the larger diameter tubes which are a part of the seal plate (f). The other tube in the seal plate is for exhausting the flowing ambient from the S/E tube. The seal plate is sealed with an O-ring to the main quartz body (g) of the S/E tube. An electrical plate (h), containing a multi-pin feedthrough for the cell connections, similarly seals against the second port of the tube body. Two joint clamps (i) secure the plates to the port flanges.

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*Reference 2, pp. 5-7

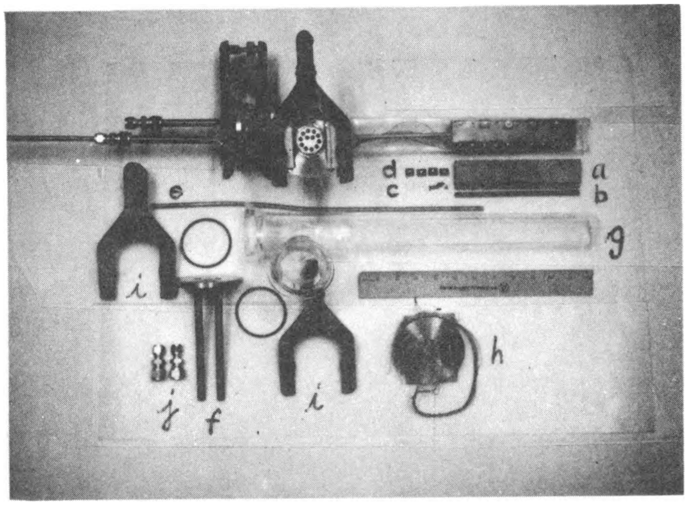

Figure 1A -- View of an assembled stress/evaluation tube (top) and its component parts.

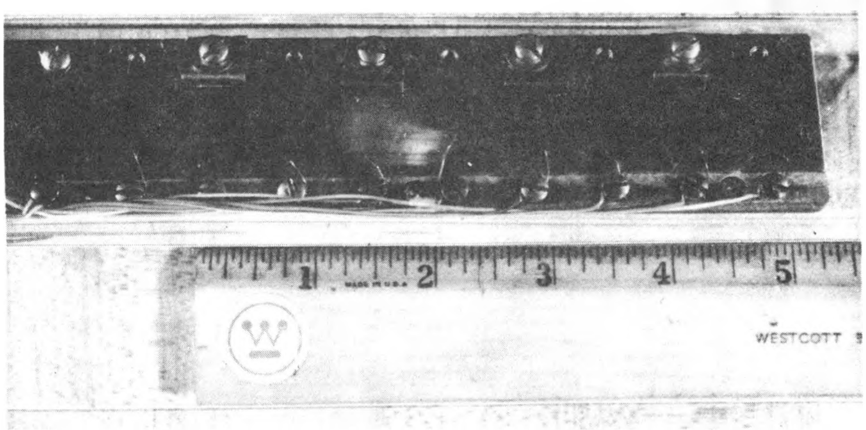

Figure 1B -- View of the cell mounting block, showing clips (d) and spring contacts (c) for individual cells.

With the arrangement shown in Figure 1, the part of the S/E tube in which the cells are mounted can be inserted into a tubular furnace. This allows in-situ annealing of the cells in hydrogen prior to aging or aging of the cells at elevated temperatures. Of the three new S/E tubes that were recently assembled, one is not intended for use in a tubular furnace. That tube has a shorter quartz body for the substrate support block and an overall length of approximately 38 cm, allowing it to be used inside a humidity chamber. In this way we expect to obtain information on the temperature and humidity acceleration of degradation mechanisms in the Cu_2S/CdS cells.

3.2 Humidity Control of Flowing Gas Ambient

In our earlier work with flowing gas ambients of high humidity, we used a very simple system. The gas in question was bubbled through distilled water in a Pyrex flask and the gas above the water in the flask was conducted to the gas input line of the S/E tube. Exhaust gas from the S/E tube was conducted into a sealed plastic box containing an Abeon hygrometer to indicate the water content of the gas. The atmosphere in the box was exhausted to the room. Adjustment of the gas flow rate was made by changing the output pressure of a control valve on the gas supply tank.

In order to control the humidity of the S/E tube ambient better, we have assembled the system shown diagramatically in Figure 2. The humidity meter box is installed in the feedline for the S/E tube. A micrometer valve (MV #1) determines the rate of gas flow through the bubbler. A second micrometer valve (MV #2) allows bleeding some dry gas into the monitoring chamber for better control of the humidity. During aging, valve V1 admits the humidified gas to the S/E tube (valves V2 and V3 are closed). The exhausted gas passes through valve V4 (V5 is closed) and into the exhaust water bubbler which acts as a seal.

Prior to aging, the S/E tube can be fed with hydrogen during preliminary measurements. In that case, only valves V3 and V5 are

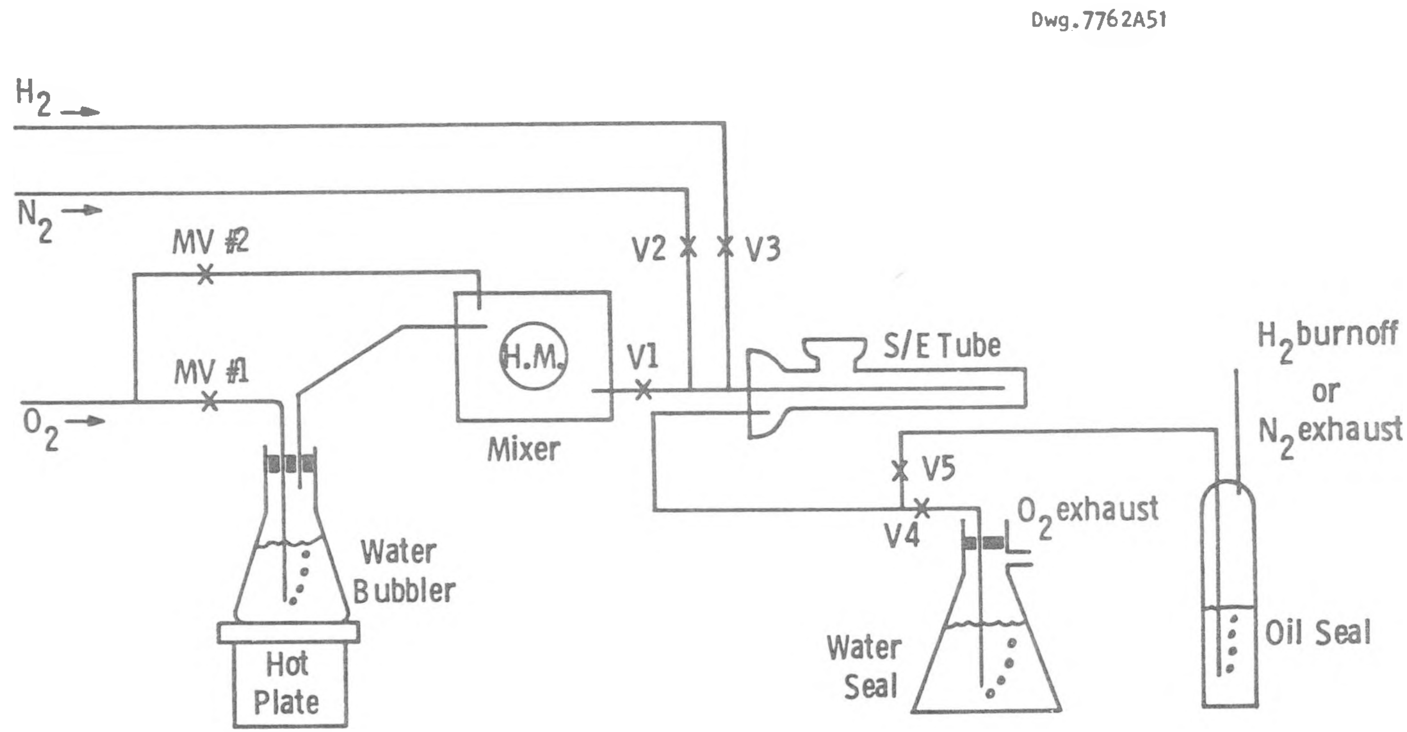

Figure 2 -- Schematic diagram showing gas-handling details for control of the ambient in the S/E tube.

open. The hydrogen is exhausted through the oil bubbler and is burned at the bubbler outlet. Nitrogen is flushed through the S/E tube and the downstream lines, which carry hydrogen both before and after hydrogen is used. This prevents the generation of small volumes of explosive O_2/H_2 mixtures.

With the arrangement shown in Figure 2, cells can be loaded, annealed in H_2, and aged and evaluated in wet O_2 without exposure to the atmosphere. Furthermore, there need be no intervening intervals of exposure to a stagnant ambient during which uncontrolled surface reactions might affect the devices under test. For our earlier work, the aging and evaluation of the cells were done in different rooms. During evaluation, the S/E tube was valved off and the tube ambient was not controlled as it is currently.

3.3 Modulating Tunneling in Cu_2S/CdS Cells

As described in Section 2.2, there are two manifestations of degraded cell performance associated with aging in wet oxygen: monotonic reduction in J_{sc} at constant illumination and changes in the diode opposing current behavior which appear to fit the model of electron tunneling from the CdS to the Cu_2S via deep donor states located near the Cu_2S. With regard to the latter effect, there is presently no information on the origin of the tunneling states. As Hanes and Bube have noted,(4) they could be of chemical or structural origin.

From our earlier experiments we have information that may shed light on the origin of the tunneling centers. In Reference 9, we characterized the behavior of small area (6×10^{-4} cm^2) cells for different immersion times in hot CuCℓ solution during barrier formation. The cells were all produced on the same small piece of CdS film, which was unetched to eliminate complications attributable to surface texturing. After the last cells were dipped, all were heat-treated for 2 min in air at 250°C to finish the barrier processing step. The photovoltaic behavior of the best cell for each dip time is shown in Figure 3 in terms of V_{oc} and I_{ph} behavior as the intensity of light incident on the cells was varied. We have extracted the values for slope and photocurrent intercept at $V_{oc} = 0$ for each of the lines fitted in Figure 3. The values are associated, respectively, with the parameters $a_i q$ and I_o in the behavior predicted by the model of Haines and Bube:

$$I_{sc} = I_o[\exp(qa_iV_{oc})-1].$$

Figure 4 shows the data plotted, along with the regression line we previously fitted (Reference 3, Figure 5), to data for large cells aged in wet oxygen.

The data of current interest appear to fit the regression line reasonably well, except for a consistently larger deviation in the value of J_o for the cells with longer immersion times during barrier formation. This can be explained by an increase in area providing opposing current as the copper sulfide layer penetrates down grain boundaries. Using the model of Rothwarf,[(10)] we estimate a rate of penetration down the boundaries of grains about 1 μm in diameter, which would be 30 times greater than the rate of Cu_2S growth on the top grain surface. Rothwarf estimated a factor of about 50 enhancement for similar processing conditions.

If we focus on the change of $a_i q$ with duration of the CuCℓ immersion step, the parameter $N_{d,eff}$ is the density of ionized donors in the CdS space charge region adjacent to the Cu_2S layer. That density determines the electric field for the region in question, which affects the barrier for electron tunneling to and from the deep donor sites. Haines has previously pointed out that the value of $N_{d,eff}$ generally decreases with increased annealing time after barrier preparation. This decrease was attributed to the creation of Cu-related acceptor centers in the space charge region as copper diffusion from the Cu_2S took place. In the present case we interpret the change in $a_i q$ values to be

Curve 732350-A

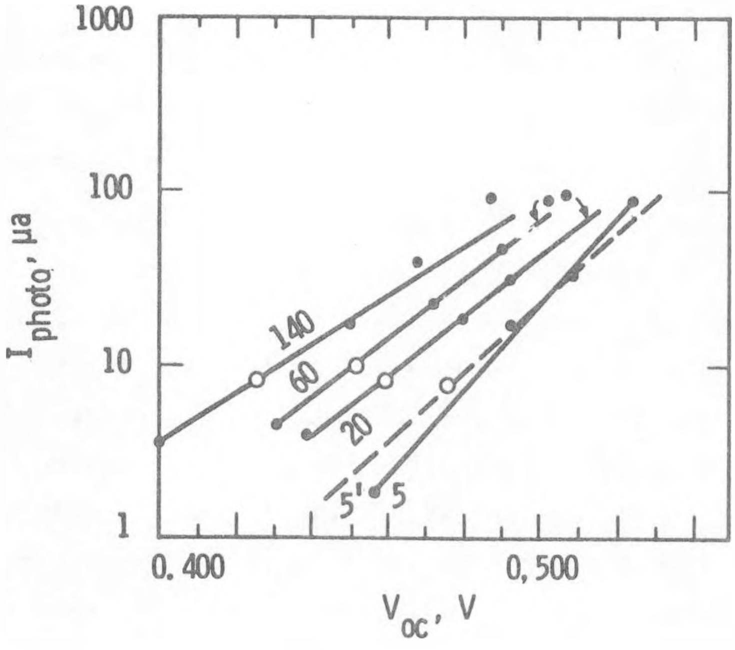

Figure 3 -- Photovoltaic behavior for small, thin-film cells produced by varying the immersion time in CuCℓ solutions during Cu_2S layer preparation.

Curve 732349-A

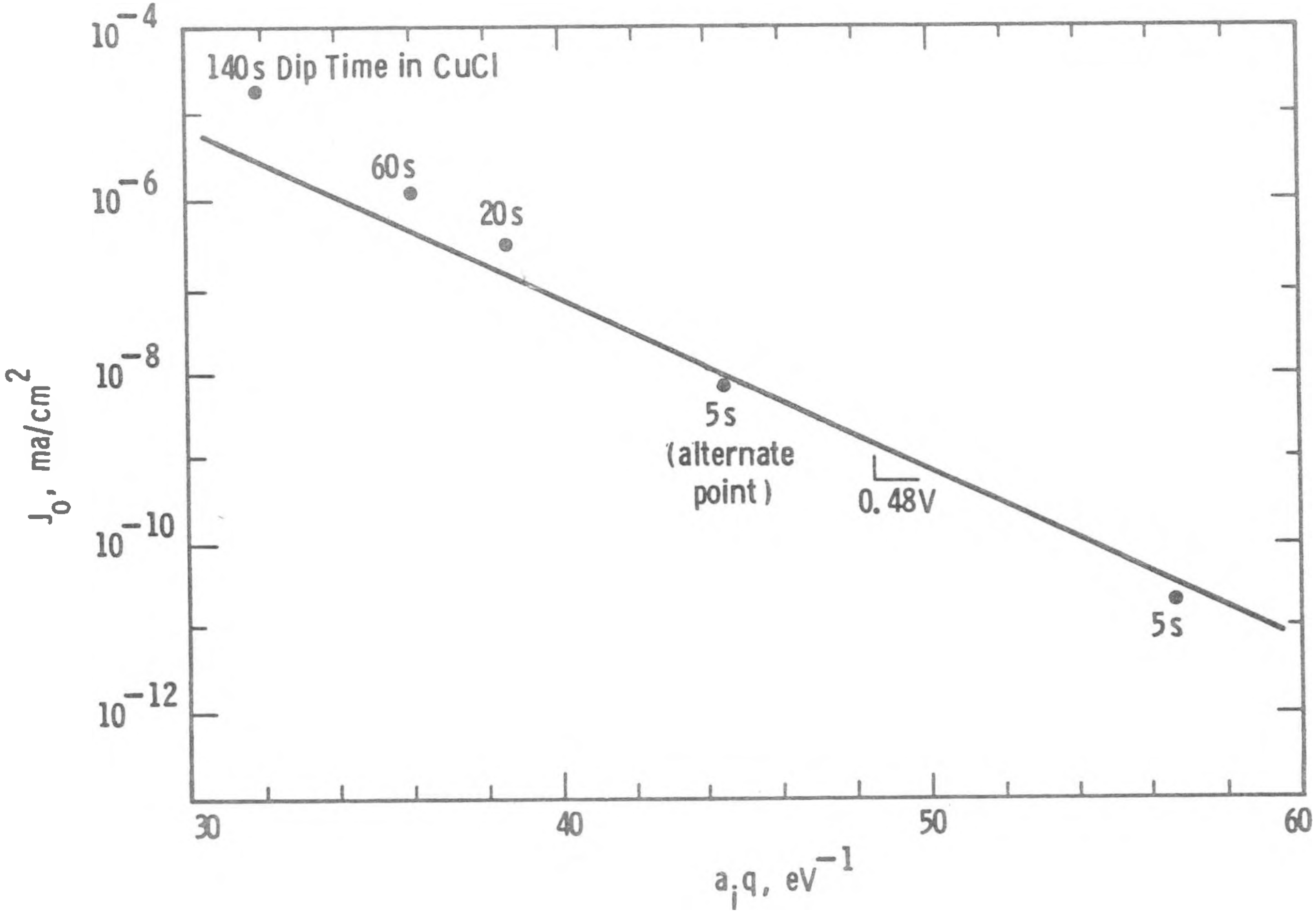

Figure 4 -- Values of $a_i q$ and J_o from Figure 3, showing the relationship to a regression line from Reference 3, Figure 5.

associated with an increase in $N_{d,eff}$ as shown in Figure 5. The total increase is not very large, ranging from 8 to 35% at most, depending on the value of a_{1q} chosen to characterize the cell receiving the shortest $CuC\ell$ immersion.

The increase of $N_{d,eff}$ with time of immersion in the $CuC\ell$ solution could be due to any of several effects. It might be caused by an increase in the density of shallow donors with depth into the CdS film as a result of the CdS preparation conditions. A decrease in the density of Cu-related acceptors for the conditions of the longer immersion time would have the same effect. A less complicated hypothesis is that the increase in $N_{d,eff}$ reflects an increase in the density of the deep donors involved in the tunneling. Such an effect would be consistent with a structural origin for the deep donors, e.g., due to the lattice mismatch between the Cu_2S and the CdS. The lattice strain resulting from such a mismatch should increase with the thickness of the Cu_2S layer. A mechanism of this sort might be sensitive to deliberate structural modifications of the Cu_2S, e.g., as a result of the Bogus treatment to alter the stoichiometry of the Cu_2S layer or of ion implantation and annealing. If the density of deep donors tunneling sites could be reduced during barrier formation or subsequent treatment, it may be possible to lessen the degrading effect of oxygen and water on opposing current behavior in Cu_2S/CdS cells.

Curve 732351-B

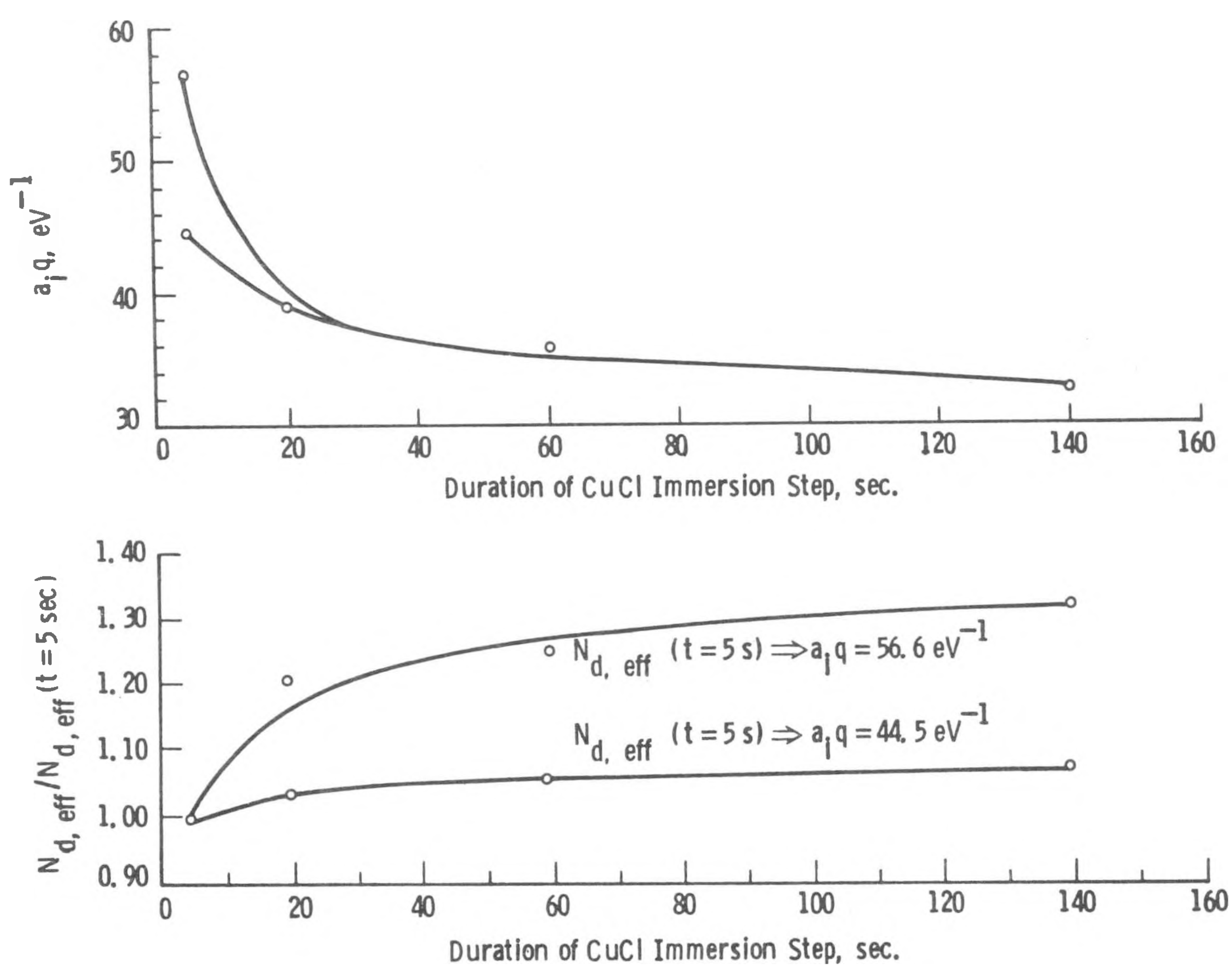

Figure 5 -- Influence of CuCℓ immersion time on parameters which control tunneling-limited opposing current in Cu_2S/CdS cells.

4. PLANS

During the next period, we will select cells for high values of J_{sc} and begin another series of aging experiments in flowing oxygen with high relative humidity (> 90%). Our main emphasis will be to characterize better the kinetics of the tunneling effects in degrading V_{oc} behavior.

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6. ACKNOWLEDGMENT

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