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

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

J. R. Szedon

ABSTRACT

In contrast to our original findings, there was no rapid component of short-circuit current loss due to aging in moist oxygen in the present case. This may be related to the difference in annealing histories of the two groups of cells. For the first 54 hrs of aging, the present results can be fitted using a single time constant with a value of about 30 hrs. We obtained information on the rate of change of the effective density of donors in the CdS space-charge region, which modulates the tunnelling opposing current that controls open-circuit voltage behavior in these cells. We observed an increase in the density of donors of about 70% during 400 hrs of aging. The increase could be fit to an exponential function with a time constant of about 35 hrs. This is of the same magnitude as the time constant associated with the degradation of short-circuit current during aging. At this time we do not have enough information to comment on the significance of this similarity.

1. SUMMARY

During this period, we continued studies on the aging of copper sulfide/cadmium sulfide solar cells in wet oxygen at room temperature. We selected cells with high performance which had been originally annealed in hydrogen at 150°C for 600 hrs. Our previous aging studies involved cells selected from groups that were annealed for about 150 hrs.

Short-circuit current and open-circuit voltage data were obtained as the basic illumination level (90 mW/cm^2) was reduced by factors ranging to about 20 with neutral density filters. These measurements were made both before and after aging of the cells in a flowing, wet (about 95% R. H.) oxygen ambient. The most dramatic effect, as we reported earlier, is the reduction in short-circuit current. In contrast to our original findings, there was no rapid component of current loss in the present case. For the first 54 hrs of aging, the current results can be fitted using a single time constant with a value of about 30 hrs.

Earlier we noted that aging produced changes in the opposing current behavior of Cu_2S/CdS cells which could be interpreted in terms of a tunnelling-controlled model. In the current work, we continued to explore use of this model to obtain information on the rate of change of important parameters in the model, particularly the effective density of all donors in the CdS space-charge region.

There are at least three sources which could influence the effective density of donors: the shallow donors which control the resistivity of the CdS film as a whole, the acceptors associated with copper diffusion into the CdS from the copper sulfide layer during heat treatments, and the deep donors (as yet unidentified) through which the tunnelling actually occurs. Of these sources, it is unlikely that the

first two are affected during aging in our experiments. One would expect them to be stable under the aging conditions, since their formation is associated with high-temperature processing steps. Until another species is identified, we will associate aging-related changes in the effective density of donors in the CdS space-charge region with the deep donors.

We observed an increase of about 70% in the effective donor density within the space-charge region during 400 hrs of aging. The increase could be fitted to an exponential function with a time constant of about 35 hrs. This is of the same magnitude as the time constant associated with the degradation of short-circuit current during aging. At this time we do not have enough information to comment on the significance of this similarity.

During the first 50 hrs of aging, only the effective density of donors appears to change, as described above. This does not involve modifications in the energy relationships important to the current-controlling mechanism. In this regime, the state of the opposing current mechanism can be described as a point along a universal curve which relates the opposing current pre-exponential term to the effective density of donors. Data for longer aging times may require more complex explanations.

During the next period we will continue with aging experiments using cells given normal annealing (about 150 hrs long) rather than using cells, such as those in the current study, which were subjected to very long anneals. In addition we will attempt to modify some cells by ion implantation to determine if their aging behavior can be improved.

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 which preceded the current one. During the first phase, the emphasis was on identifying and duplicating the critical steps for fabricating 9% efficient cells. The achievement of these goals in 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 alternative methods of grid-electrode formation to reduce the cost associated with using thick, evaporated gold grids.

Having defined a reproducible processing method for fabricating high-efficiency cells and having preliminarily identified several major degradation effects in these cells due to the combined effects of moisture and oxygen, we are now in the second quarter of the most recent phase of the program. Its focus is to improve the stability of cell performance by several means which are described next.

2.3 Approach

Presently, we are focussing on issues involving the stability of Cu_2S/CdS thin-film solar cells. Our primary goal is to improve the stability of these cells. We first determined which device characteristics are the most important indicators of degradation mechanisms. From our earlier work, the loss of short-circuit current capability and the changes in open-circuit voltage due to tunnelling control of diode opposing current seem to be the most significant sources of cell degradation under storage conditions.

The second aspect of our approach to the stability problem is to determine the kinetic behavior of the short-circuit loss and of the tunnel model parameters which are involved in the changes in opposing current behavior. Part three of the approach is to determine whether encapsulation or modification of the cells can significantly reduce the rate at which the photovoltaic performance degrades. The combination of water vapor and oxygen appears to be necessary for the degradation we have observed. By slowing the ingress of either species or by denying them opportunities with the basic cell materials, we should inhibit the degradation of cell performance.

We feel this approach addresses for the first time the stability issue from the viewpoint of basic and empirically meaningful stress and evaluation conditions. The lack of a resolution to the stability problem in these cells earlier has probably hampered their acceptance as practical, albeit developmental, low-cost solar cells. Although the present emphasis is on the copper sulfide/cadmium sulfide thin-film cell, the understanding to be gained by following the approach outlined here should be valuable in relation to other heterojunction cells, such as those incorporating copper indium diselenide.

2.4 Program Tasks

The current phase of the program has three tasks:

Task 1. Identify major degradation mechanisms. This task is being addressed by subjecting cells to selected conditions of temperature and moisture content of the gas ambient, then characterizing the performance of the cells as a function of time.

Task 2. Improve environmental stability by encapsulation. A baseline encapsulation method will be used to determine if significant improvements in stability are afforded in comparison to unprotected cells studied in Task 1.

Task 3. Improve the intrinsic stability of Cu_2S/CdS solar cells. Modification of the copper sulfide layer will be attempted by several means, including ion implantation. Evaluations of the effects of these modifications will be made in terms of cell behavior during aging.

3. PROGRESS

3.1 Experimental Procedure

During this period, we continued studies on the aging of copper sulfide/cadmium sulfide solar cells in wet oxygen at room temperature. For these experiments we selected cells with high performance. The cells had been originally annealed in hydrogen at 150°C for 400 hrs. Our previous aging studies involved cells selected from groups which were annealed for about 150 hrs. We were interested in determining if this difference in the duration of the high-temperature annealing of the cells influenced their aging behavior.

The cells were installed in the stress/evaluation (S/E) tube which allows measurement of the cells and exposure to a variety of flowing gaseous ambients without exposure to the atmosphere. Insulated clips were used to hold the cells against the copper substrate block and spring wire contacts were made to the grid electrodes. Details of the S/E tubes are given in the Tenth Technical Progress Report.[1] As in previous studies, we characterized cell behavior using a Digital Equipment Corp. MINC-11 system to obtain, store, and analyze the data.

The S/E tube was closed and purged with house nitrogen to displace air. Hydrogen was introduced and the cells were held at room temperature for several hours before in-situ characterization was done. Initially, short-circuit current and open-circuit voltage data were obtained as the basic illumination level (90 mW/cm^2) was reduced by factors ranging to about 20 with neutral density filters. We also characterized the cells in the presence of bias light from a microscope illuminator which passed through either red or blue glass filters (Corning #2408 and #5900, respectively). This was done with the expectation that aging might affect the spectral sensitivity arising from centers in the CdS space-charge region, as reported by Haines and Bube.[2]

After the initial measurements were made, the S/E tube was purged with dry house nitrogen, and flowing wet (about 95% R. H.) oxygen was introduced. Detailed measurements of the type described above were made after intervals of 1 to nearly 400 hrs. When the short-circuit current had degraded appreciably due to aging, additional measurements were made with the simulator-to-cell distance being reduced to achieve higher illumination levels and to exercise the cells at current levels near the original level for 90 mW/cm^2.

3.2 Results

3.2.1 Short-Circuit Current Reduction

The most dramatic effect of aging in moist oxygen, as we reported earlier,[3] is the reduction in short-circuit current. Results for two cells in the present series are shown in Figure 1. In contrast to the original findings in reference 3, there appears to be no rapid component in the loss mechanism. For the first 54 hrs of aging, the results can be fitted in each case using a single time constant with a value of 25 to 32 hrs. The data for longer periods of aging (to 400 hrs) suggest that a component of short-circuit current loss having a much longer time constant may be present. An accurate assessment cannot be made from the present data.

3.2.2 Changes in Opposing Current Behavior

In the Ninth Technical Progress Report[4] we noted that aging produced changes in the opposing current behavior of Cu_2S/CdS cells which could be interpreted in terms of a tunnelling-controlled model originally proposed by Haines and Bube.[2] Detailed data for one of the cells in the current series are shown in Figure 2 for the purpose of a similar interpretation. While we saw some minor effects of bias light on the cell behavior, these were not as striking as those reported by

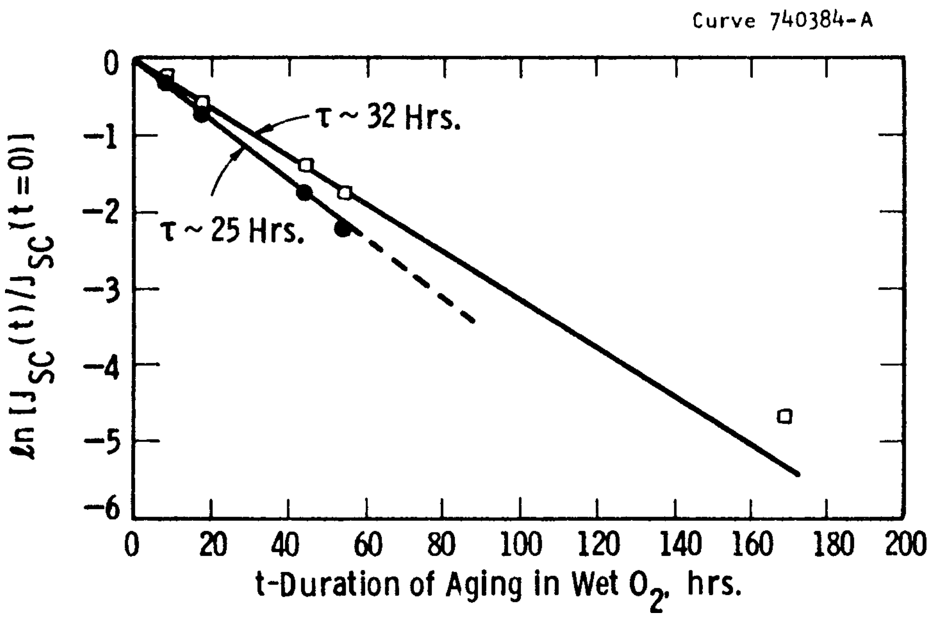

Figure 1. Effect of flowing wet oxygen at R. T. on short-circuit current capability (at ~ 90 mW/cm^2 irradiance) of two cells.

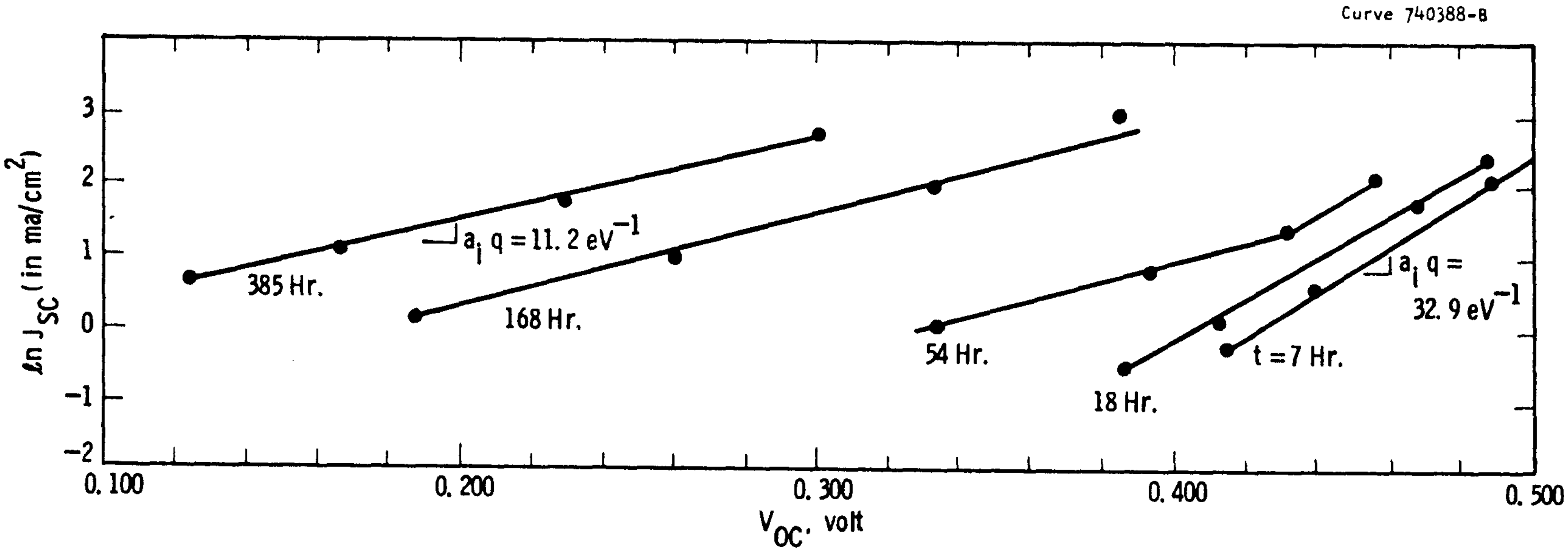

Figure 2. Changes in opposing current behavior at selected intervals during the aging of a cell in flowing wet oxygen at R. T.

Haines and Bube in reference 2. The results given in Figure 2 and in the remainder of the report are for the case of no bias light.

For each aging interval, the data of Figure 2 were fit by least squares linear regression to the expression:

$$J_{SC} = J_0 \{\exp(qa_i V_{OC}) -1\}.$$

The respective values of J_0 and qa_i are shown plotted in Figure 3. Through 54 hrs, the data are fitted by the linear regression to the solid line which has a slope of -0.49 v and an intercept, ln J_{00}, of 1.60. These parameter values are remarkably similar to those deduced for the results we obtained earlier in Figure 5 of reference 4. For another cell in this test series, similar results were obtained on treating the opposing current behavior in terms of the tunnelling model. These are shown in Figure 4. Our interpretation of the significance of these results is given in the following section.

3.3 Discussion

3.3.1 Degradation of Short-Circuit Current on Aging

On this program we have determined that two major effects occur during the aging in wet oxygen of unencapsulated Cu_2S/CdS solar cells: 1) progressive loss of short-circuit current and 2) changes in the diode opposing current, which appears to be due to modulation of electron tunnelling that takes place via deep-donor states in the space-charge region. Previously, we observed that the degradation of short-circuit current had a time dependence fitted by two exponential functions with time constants differing by a factor of about 10 (4 hrs vs. 35 to 40 hrs).[(3)] In the current studies, effects of a short time constant are not detectable (compare Figure 1). We also demonstrated earlier that, under the aging conditions used, the loss in short-circuit current was not ascribable to changes in the optical absorption properties of the copper sulfide layer. Partain et al. have subsequently confirmed these

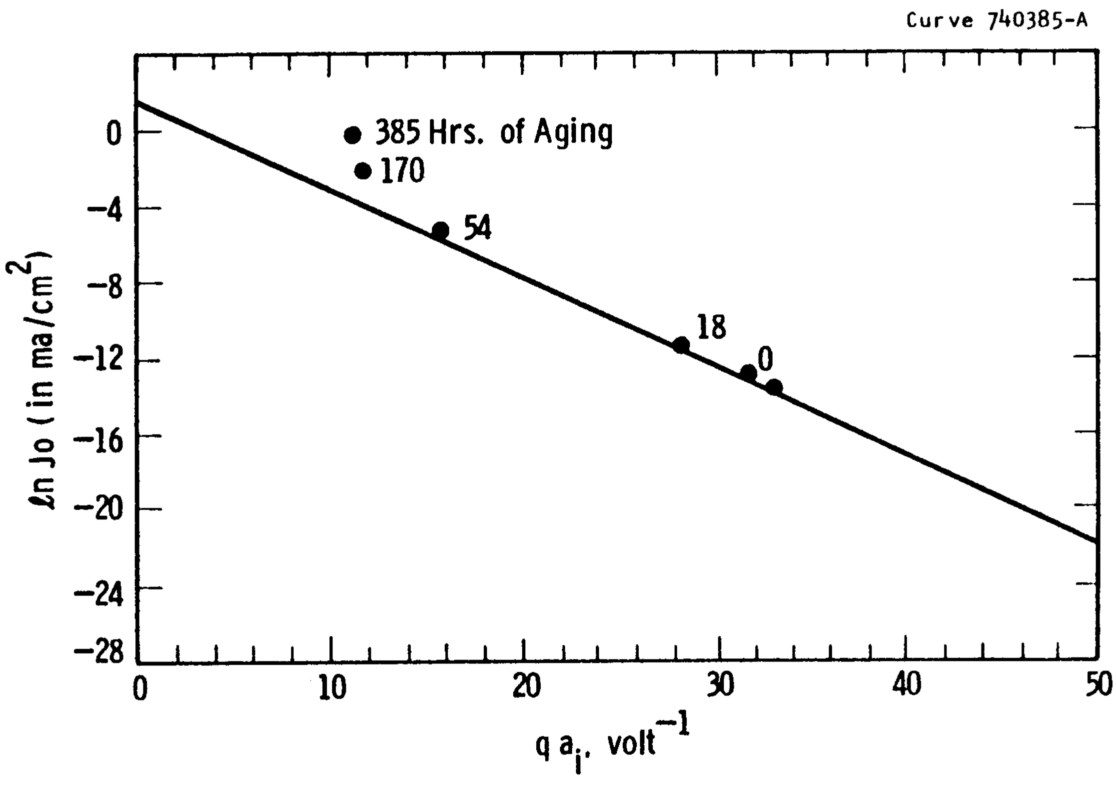

Figure 3. Co-variational behavior of ln J_0 and qa_i terms which supports the hypothesis of changes in tunnelling-controlled opposing current for the cell-aging results.

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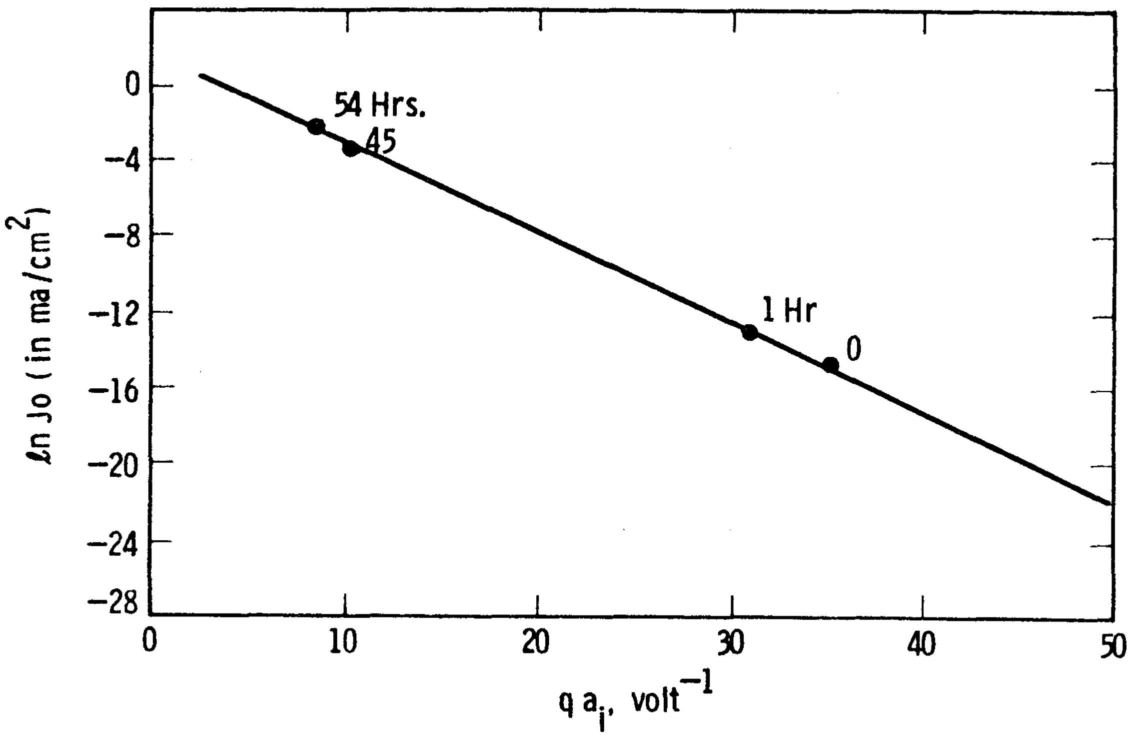

Figure 4. Results similar to those of Figure 3 for another cell.

observations.[5] They have associated the photocurrent loss with a significant reduction in the diffusion length of minority carriers in the copper sulfide layer during aging. Peterson and Washburn proposed that the formation of dislocation arrays within the copper sulfide on oxidation could attenuate the collected photocurrent by as much as 80%, through recombination.[6]

We have noted earlier, but not reported, that cells exhibited changes in the dynamic behavior of their short-circuit current degradation. This behavior was controlled by two time constants during the first aging cycle. After recovery by high-temperature annealing in hydrogen, the cells degraded subsequently in photocurrent capability, but only the longer time constant applied. In light of the work by Partain et al., this could be indicative of surface recombination influences on the faster loss mechanism. Surface recombination mechanisms could be very sensitive to particular heat treatments, such as the long anneal times of the cells used in the current study or to the combination of aging and short annealing which were done in some cases.

3.3.2 Kinetics of Aging Effects on Opposing Current

In order to identify, understand, and eliminate degradation mechanisms in solid state devices, it has generally been appropriate to characterize the kinetic aspects of the degradation. Although we identified changes in opposing current behavior as an aging effect earlier, a kinetic analysis became meaningful only after we associated the tunneling mechanism of Haines with these effects. That association was made in the Ninth Technical Progress Report on this program.[4] Subsequently, in reference 1 we proposed that structural effects attending the formation of the copper sulfide layer were involved in modulating the tunneling control of opposing current behavior in these cells.

Our preliminary results involved data for short-term aging, about 22 hrs. In terms of the simplest physical view of the tunneling mechanism, those aging results appeared to involve a change in the effective density of all donors in the CdS space charge region. The effective density of donors appeared to decrease within the first 4 to 5 hrs of aging, and subsequently return after 22 hrs to near the original value.

There are at least three sources which could influence this effective density of donors: 1) the shallow donors which control the resistivity of the CdS film as a whole, 2) the acceptors associated with copper diffusion into the CdS from the copper sulfide layer during heat treatments, and 3) the deep donors (as yet unidentified) through which the tunnelling actually occurs. Of these sources, it is unlikely that the first two are affected during aging in our experiments. One would expect them to be stable under the aging conditions, since their formation is associated with higher temperature processing steps, namely 220°C for the CdS deposition and 150°C for the barrier annealing step. Until another species is identified, we will associate aging-related changes in effective density of donors in the CdS space-charge region with the deep donors.

An analysis of the data given in Figures 2 and 3 was made in terms of the tunnelling model. From equation 4 in reference 4, the value of the term $a_i q$ is inversely proportional to the square root of the effective density of donors in the CdS space-charge region adjoining the copper sulfide layer. For the cell in question, the effect of aging on the effective density of donors, normalized with respect to the value before aging, is shown in Figure 5.

As for the earlier results interpreted in this way (reference 4), in the very early stages of aging there appears to be a decrease in the effective density of donors during the earliest stages of aging. This manifests itself as a slight improvement in the open-circuit voltage at constant short-circuit current. For the present case,

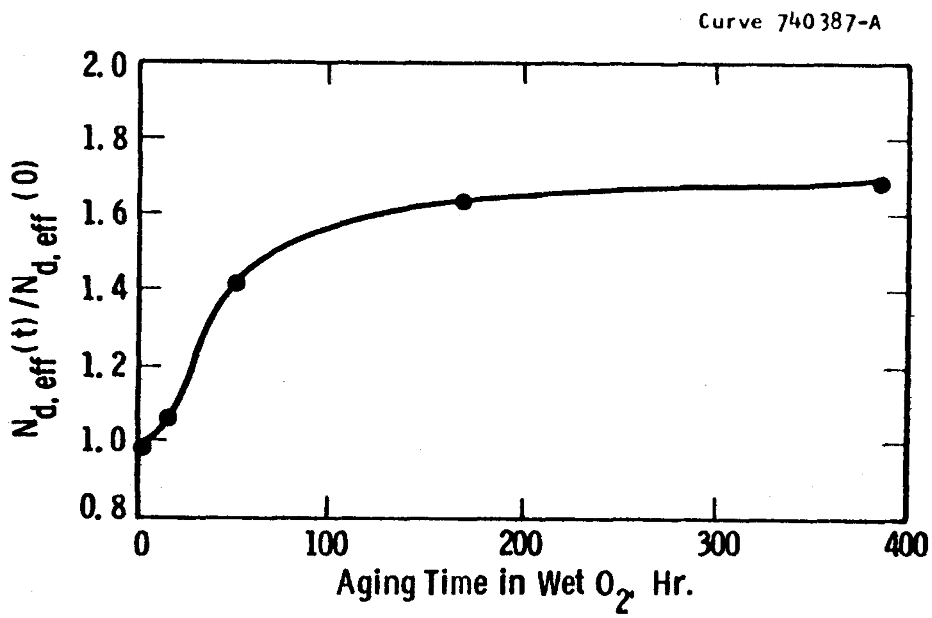

Figure 5. Time dependence of the effective density of donors in the space-charge region, as inferred from the data for qa_i in Figure 3.

however, the reduction in net donor density was much smaller than that inferred for the earlier tests (< 5% vs. ~ 50%). This difference may reflect the differences in the duration of the annealing steps which preceded the aging tests.

If the curve of Figure 5 is treated as an exponential function, it can be fitted using a time constant value of about 35 hrs. We note the similarity of this value to that obtained for the degradation kinetics of the short-circuit current in this cell, as shown in Figure 2. More work will be needed to determine if this similarity is significant.

Before finishing this discussion of the kinetic aspects of the aging behavior observed in the current studies, we should look at another aspect of the tunnelling model. With regard to Figure 3, the current aging results in terms of values for $\ln J_0$ and $a_i q$ agree very well with earlier applications of the model, in the sense that they can be fitted by a single straight line. The slope of that line is determined by the energy of the tunnel donor site and by the tunnelling barrier height at zero temperature. The intercept of the line for an $a_i q$ value of zero gives the tunnelling source current which depends on a number of factors, e.g., the densities of the deep level donors, of levels in the copper sulfide available for tunnelling electrons, and of electrons in the CdS conduction band. From Figure 3 we may consider that none of the energy relationships or the important state densities changed significantly during the first 50 hrs of aging for the cell in question. The tendency for points representing longer aging times to lie above the fitted line could be accommodated by a change in intercept alone (involving no change in the energy scheme of the cell). More data will be required to determine if this relatively uncomplicated view is justified.

4. PLANS

During the next period we will continue with aging experiments using cells given normal annealing (about 150 hrs long) in hydrogen rather than using cells, such as those in the current study, which were subjected to very long anneals. In addition, we will attempt to modify some cells by ion implantation to determine if their aging behavior can be improved. There is expectation of improvement if the effects of water and oxygen can be moderated in the presence of a reactive chemical species without introducing undesirable structural or electronic effects.

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