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

Fifth Technical Progress Report for the Period July 13—October 12, 1980

MASTER

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November 5, 1981

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Westinghouse R&D Center
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Solar Energy

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

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H. C. Dickey

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13 July 1980 to 12 October 1980
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November 5, 1981

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1. SUMMARY

The Westinghouse R&D Center is engaged in a program to develop and document cell-processing methods for 9% efficient, low-cost Cu_2S/CdS thin-film solar cells. A new phase of work was begun during this quarter with an expansion of the scope of the program. Three new tasks are currently being addressed: (1) establishing the reproducibility of a wet-chemistry processing sequence for 9% efficient cells, (2) improving the performance of cells in terms of efficiency and stability, and (3) developing low-cost electrode gridding methods.

Work was initiated in all three task areas, but the emphasis during this quarter was on improving the accuracy of substrate temperature control during CdS deposition. This was achieved by welding thermocouples to a molybdenum foil tab which was subsequently welded to the copper foil substrate. With this arrangement, the possibility was reduced for false, high-temperature indications provided by thermocouples poorly welded directly to the copper. Structural features of the CdS films were consistent with control of the substrate temperature at ~ 220°C, as desired.

Improvement of cell efficiency and stability requires better knowledge of optical and electronic properties of the Cu_2S films used in cells. Direct measurement of these properties requires removal of the copper foil substrate for optical transmission characterization. Simple etching of a window in the substrate is not acceptable since the CdS film cracks around the periphery of the window. Other methods for providing the required specimens or alternate measurement methods will be explored further.

Encouraging cell performance results were obtained with evaporated grids which consisted of two layers: a thin layer of either

gold (840Å) or copper (~ 60Å) on the Cu_2S surface and a 2.5 μm thick overlayer of lead for high electrical sheet conductance. From preliminary cell results for short annealing times, the best cells with multilayer grids were only 15 to 20% lower in efficiency than control cells using 2.5 μm thick gold electrodes. Further improvements in cell performance might result from additional annealing. A more detailed analysis of cell performance will be presented after additional annealing is done.

2. INTRODUCTION

2.1 Objective

The objective of this program is to develop and document cell-processing methods for 9% efficient Cu_2/CdS thin-film solar cells and to assess selected alternate routes for achieving cells with 10% or higher efficiency. Specifically, the current phase is concerned with (1) improving base-line processing methods to give greater control over the reproducibility of cell performance, (2) investigating means to make more stable, high-efficiency solar cells, and (3) evaluating alternate methods of grid-electrode formation to reduce the cost of thick evaporated gold grids.

2.2 Contract Tasks

Earlier work on the program has resulted in the completion of program tasks described in Ref. 1. A contract modification which became effective on September 13, 1980 calls for an expansion of the original scope of work on this program, to include the following three tasks:

Task 1. Establish the reproducibility of a wet-chemistry process sequence for 9% cells.

Task 2. Explore methods for improving cell performance.

Task 3. Develop low-cost gridding methods.

2.3 Technical Approach

In earlier work on this contract, critical aspects of cell fabrication were identified by comparing process-step details, material characteristics, and cell performance results for processing sequences used at Westinghouse and those used at the Institute of Energy Conversion of the University of Delaware.

Pursuit of the three new tasks on this program requires the use of new technical approaches. First, further improvement of base-line cell processing is to be pursued. The main emphasis is to be on improving control and reproducibility of important processing parameters. Chosen as examples are substrate temperature during CdS deposition and the wet-chemistry conditions attending formation of the Cu_2S layer during immersion of the CdS film in a hot CuCℓ solution. Statistical assessment of cell performance results is to be used in evaluating the efficiency of new processing methods.

The second aspect of the new approach involves improved cell performance. It is clear that a better understanding of cell behavior is required to support work on both higher efficiency and on improved stability. We feel that important advances can be made only if more basic characterizations are made of the Cu_2S layer in a working-cell context. We expect to try several methods to permit characterization of the optical transmission of Cu_2S layers used in actual cells. In addition, we will be exploring the use of plasma hydrogenation as an alternative to open-tube annealing in hydrogen, which is currently being used to optimize cell performance.

Finally, we will be trying two methods to reduce the cost of grid electrodes for Cu_2S/CdS cells. The highest performance cells reported to date use thick (~ 2.5 μm) gold electrodes formed by evaporation through an aperture mask. Electroplating of gold directly on the grid areas will be tried. This will reduce the amount of gold expended for each cell to less than 10% of that for the current method. A second approach is to use a multi-layer grid. A thin layer of gold or copper will be used for contacting the Cu_2S region. A second thick layer of a material such as lead will be used to provide an adequately high sheet conductance for the grid electrode. The use of the gold is a conservative extension of current practice. Thin copper layers are reported as improving cell performance by maintaining the stoichiometry of the Cu_2S surface.(2)

3. BASE-LINE PROCESSING

3.1 Cadmium Sulfide Deposition

During the first half of the present quarter, improvements to the evaporator were made under Westinghouse sponsorship while contractual details for the current work were being approved. The evaporator for CdS depositions was upgraded by extensive cleaning of the system and tooling, by reducing the size of the bell jar, and by repairing critical valves. Faster pumping and lower system pressure prior to evaporation have been achieved.

A new method of applying thermocouples to the foil substrates has been devised. The earlier practice of welding the thermocouples directly to the copper gave variable results in terms of the mechanical strength of the weld and in terms of tracking between two couples on the substrate.

With the new method, the couple is welded to a molybdenum foil tab, which can be done more reliably than welding to copper. The tab is then welded to the copper foil. There is good tracking of temperature reading between two thermocouples attached in this way.

We feel the new thermocouple method will reduce the variability of the actual substrate temperature during CdS deposition. If erroneously high substrate temperatures result from poor thermocouple monitoring methods, then actual substrate temperature well below the desired value of $\sim 220^{o}C$ could cause bimodal grain-size distributions.*

Cleaning of the vacuum system and improving the method for mounting substrate thermocouples for substrate temperature monitoring

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*See Fig. 7a of Ref. 1 for an example of a film with a bimodal grain size distribution due to low substrate deposition temperature.

resulted in improved films. Grain structure, as revealed by Cu_2S formation and removal, did not indicate a bimodal grain-size distribution. Through-the-film resistivities of films, determined using indium-dot electrodes, were in the 10 to 20 ohm-cm range, somewhat higher than for films prepared earlier. Of five of the new CdS films, three gave cells with efficiency values of 6.2 to 7.7%, an acceptable range.

3.2 Wet-Chemical Processing

One of our major concerns with conventional cell processing is the step for forming the Cu_2S layer. There is poor control over conditions of the transfer from the hot CuCℓ solution to the rinse which follows. During the transfer period, exposure to air may promote cupric ion formation in the CuCℓ solution retained on the cell surface. This is generally undesirable since precautions are taken in preparing the solution to eliminate cupric ions. An additional concern is the possibility that the concentration of the film of CuCℓ solution retained on the cell surface may change as water evaporates.

Two approaches could be taken to minimize the possibilities discussed above: (1) use of a jet of argon gas to remove the solution from the surface while the cell was within the argon atmosphere which is maintained over the CuCℓ bath, and (2) transfer of the cell, while immersed in a small volume of CuCℓ, using a shallow container. We chose to explore the latter approach first, since it was more easily implemented.

After other cells had been processed conventionally, one group of four cells was processed in a Petri dish. The CdS film was taped inside the dish. The cells remained under the CuCℓ solution during the transfer, and the solution was diluted during the first rinsing stage. Although these cells were comparable in terms of short-circuit current density to the control cells processed conventionally on the same CdS film, their open-circuit voltage values were about 25 mV lower. Other implementations of this approach, with special containers to minimize the amount of CuCℓ solution used in the transfer, will be tried in the future.

4. IMPROVING CELL EFFICIENCY

4.1 Background

This task requires that attention be paid to two important areas: (1) better understanding of the effects of hydrogen annealing and of atmospheric exposure on cell performance, and (2) a means for directly measuring the optical and electrical properties of the copper sulfide layers used in actual cells. To treat the former area we have designed a sealed ampoule that will allow heating and testing of gridded cells while they are in a controlled flowing-gas ambient. This arrangement will permit a variety of operations on the cells without exposing them to room air or uncontrolled ambient conditions. These operations include: mounting of cells, characterizing their photovoltaic performance, annealing in 100% H_2 at temperature of 180°C or lower, and exposing cells to wet or dry ambients of oxygen, hydrogen, argon, or nitrogen at temperatures in the 25 to 200°C range.

4.2 Characterizing Cu_2S Layers in a Cell Context

Improvement of cell performance and stability will require better understanding of the electrical and optical behavior of Cu_2S layers in a cell context. Without such understanding, empirical approaches to these problems will suffer from a lack of appropriate guidance. This has often been the case in the past, with overall cell performance being used as the criterion for judging the effectiveness of changes in processing or material-preparation methods. The weakness of this latter approach lies in the inability to associate with a particular cause a specific physical effect within the cell.

Models and theories exist which rationalize cell behavior in terms of Cu_2S properties (e.g., optical absorption, minority-carrier lifetime, surface-recombination velocity), of junction parameters (interface recombination and trapping), and of CdS characteristics (space-charge region field, impurity and trapping parameters). Means do not exist, however, for extracting key information on specific physical or electronic parameters of the Cu_2S layer, in particular, from conventional measurements.

The first step in providing basic information on Cu_2S layers in cells is to produce specimens on which optical transmission measurements can be made. We have previously used single-crystal CdS substrates and made measurements of Cu_2S photocurrent, and of light transmission for specimens with a tapered thickness layer of Cu_2S. Such an approach can be used to evaluate minority-carrier diffusion length, surface-recombination velocity, and heterojunction-collection efficiency.(3)

In order to apply this approach to thin-film cells, we have begun to explore methods for forming windows of freestanding CdS films by etching away small areas of the copper foil substrate. If this is done straightforwardly, the CdS films crack around the periphery of the windows, presumably due to internal stresses. We attempted to provide additional support by mounting the copper sulfide surface of a film against a brass plate using wax. The plate had a small aperture. Etching a small window in the copper foil at the location of the brass plate aperture again revealed some cracking of the CdS at the edge of the window. We will explore other means of supporting the film at its front surface, such as epoxying the Cu_2S surface to a glass slide.

5. LOW-COST GRIDDING

5.1 Electroplated Grids

The current gridding method which has given high-performance cells uses a very thick (2.5 µm) gold grid formed by evaporating through an aperture mask. Instead of going directly to schemes in which gold is entirely eliminated, we have chosen to begin by exploring methods in which the amount of gold is substantially reduced. One approach is to selectively electroplate gold only in the grid electrode area, which is less than 10% of the total cell area. Ultimately, it may be possible to produce a multi-layer grid by electroplating with a thin layer of gold to provide intimate contact with the copper sulfide surface, and with a thicker, base metal layer for conductance. Sixteen cells were fabricated with copper sulfide barrier layers for the purpose of future experimentation with electroplating.

Experiments are planned to determine if electroplating can be done directly on the Cu_2S surface without requiring an evaporated metal layer. Additionally, it will be necessary to determine if a patterned photoresist film alone can be used for the mask for plating the grid, or if an inorganic dielectric layer such as SiO_2 must be used.

5.2 Multi-layer Evaporated Grids

A second approach to low-cost gridding is to continue with evaporation, since it is known to give acceptable results, but to evaporate only a very thin gold or copper layer as the contact to the copper sulfide. A thick layer of lead can then be evaporated through the aperture mask to complete the grid. Choice of these materials was discussed in Section 2.2.

Cells were made in this way using underlayers of gold and of copper (840 and 63Å thick, respectively) and lead top layers about 2.6 µm thick. Typical cell-efficiency values for short anneals ranged from 5.1 to 5.8%, compared with values in excess of 6% for cells with thick gold grids. These results should be considered as preliminary until those for more typical anneal durations (~ 100 hr) are available during the next quarter.

6. CONCLUSIONS

An improved thermocouple mounting method gives better control of substrate temperature during CdS deposition. By welding the thermocouple to a molybdenum foil tab, we obtain a more rugged, reliable bond than by bonding directly to the copper foil substrate. The Mo tab is easily welded to the copper. This arrangement provides more reproducible readings of copper substrate temperature. With the former method, if a poor bond was produced, the thermocouple could indicate an erroneously high temperature. Thus, actual substrate temperatures during deposition would be below the desired value of ~ 220°C. The occurrence of bimodal size distributions of the CdS grains, indicative of substrate temperatures below 200°C for the system geometry and of the CdS source evolution rates we are using, has been eliminated with the new mounting arrangement.

Straightforward attempts to provide a window for optical measurements of Cu_2S/CdS layers in thin-film cells, by etching holes in the copper substrate, have not been successful. Cracks develop in the CdS film around the periphery of the window. Such cracks preclude use of the specimens for the planned optical and electrical measurements.

Preliminary results of evaporated multi-layer grid electrodes are encouraging. Cells were made with about 2.5 μm of lead evaporated over either 840Å of gold or 60Å of copper. The best cells were 15 to 20% less efficient than cells with standard gold grids (2.5 μm thick), but further annealing in H_2 may produce an even more favorable comparison.

7. ACKNOWLEDGMENTS

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