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DEVELOPMENT OF COPPER SULFIDE/CADMIUM SULFIDE THIN FILM
SOLAR CELLS

Fourth Technical Progress Report, April 13–July 12, 1980

MASTER

By
J. R. Szedon
W. J. Biter
J. A. Abel
H. C. Dickey
F. A. Shirland

February 27, 1981

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Westinghouse R&D Center
Pittsburgh, Pennsylvania

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Solar Energy

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J. R. Szedon, W. J. Biter, J. A. Abel,
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ABSTRACT

The purpose of this work has been to identify aspects of cell fabrication and treatment which are critical for achieving high efficiency $\text{Cu}_2\text{S}/\text{CdS}$ solar cells. In approaching the problem, several comparisons, with successively increased scrutiny, were made of the effects of specific steps in two methods of cell fabrication. These methods had previously given cells of about 6% and a maximum of 9% efficiency. Three areas requiring special attention and specific means to achieve acceptable results were identified. (1) The $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction area must be minimized. If single source evaporations of CdS are made on substrates whose temperatures ($\sim 220^\circ\text{C}$) are monitored and controlled using welded thermocouples, the CdS films will have adequately large grains (grain diameter $\gtrsim 2\ \mu\text{m}$) and will not develop significant etch pits during texturing in a mild etchant solution. (2) The termination of the wet barrier processing steps must be done carefully. An acceptable termination involves minimizing the amount of cuprous chloride retained on the cell surface during transfer to a rinsing stage while providing adequate exclusion of air from the space above the surface of the cuprous chloride solution. (3) Once formed, the Cu_2S layer should not be exposed to high temperatures ($> 100^\circ\text{C}$) for long periods of time ($> 5\ \text{min}$) if surface adsorbed moisture or oxygen are present. Heat treatments in ampoules under flowing hydrogen atmospheres should be preceded and followed by periods of at least 30 minutes at room temperature in the reducing ambient. If all these precautions are taken, wet chemical barrier processing of thermally evaporated CdS films on zinc-plated copper foil substrates yields cells of nearly 3% conversion efficiency without AR coating. A well-controlled baseline cell fabrication process sequence incorporating these key factors should be an important part of the future efforts to assess cell stability and reliability, to upgrade process steps for lower cost and greater reproducibility, and for exploring means to improve cell efficiency.

1. SUMMARY

Background. The purpose of this work has been to identify those aspects of the preparation of $\text{Cu}_2\text{S}/\text{CdS}$ solar cells using evaporated films of CdS and wet chemical processing which are critical in achieving high conversion efficiency. In approaching this problem, comparisons were made with increasingly greater scrutiny between processing previously used at Westinghouse and that in use at the Institute of Energy Conversion (IEC) of the University of Delaware. The former Westinghouse procedures had produced 4 cm^2 cells of 6.3% maximum efficiency; the IEC ones had resulted in 1 cm^2 cells of 9.1% efficiency. Values of fill factor and open circuit voltage were consistently lower for the Westinghouse cells.

Fabrication at both facilities generally followed the earlier Clevite approach to cell fabrication: thermal evaporation of the CdS from a powder onto a flexible substrate, in this case a zinc-plated copper foil, etching in a heated solution of hydrochloric acid to texture the CdS surface and reduce the reflectivity of the finished cell, formation of the Cu_2S layer by a chemical exchange process during immersion of the CdS in a solution of cuprous chloride, appropriate gridding and heat treatment. Systematic comparisons of detailed differences between Westinghouse and IEC practice for implementing these steps were made on three occasions during the program. Frequent verifications were made that chemicals used in the processing were identical as regards origin and purity. Following each of the comparison surveys, the existing procedures at Westinghouse were modified to give greater conformity with the IEC methods. The results of the changes were tracked in terms of physical changes in the films and cells and in terms of photovoltaic performance of cells.

Some specimens of CdS films produced at IEC and known to produce cells there of particular, acceptable performance were included

in the processing at Westinghouse to distinguish effects on cell behavior associated with the CdS films from those related to subsequent processing. For the third stage of detailed comparison, CdS films produced at Westinghouse were processed at IEC simultaneously with IEC film samples. Subsequently, the groups of cells fabricated on both types of films were divided. Extensive heat treatments on the new groups containing cells on both types of CdS films were done at IEC and at Westinghouse to judge the comparability of the heat treatment methods at the two locations.

As a result of the approach just described a number of key factors have been identified as causing significant changes in CdS film structure and having an impact on the photovoltaic performance of $\text{Cu}_2\text{S}/\text{CdS}$ cells. These factors, together with the major unresolved issues, are treated below for the various steps in cell fabrication.

Substrate Preparation. No aspects of this step were considered to produce a significant change in CdS film structure or in cell performance when previous Westinghouse procedures were replaced by those recommended by IEC.

CdS Deposition. Films of CdS produced using single evaporation sources have a different structure than those produced with four identical sources, which was the earlier Westinghouse practice. With all other conditions being the same, the single source films have larger grain sizes and develop few deep etch pits during HCl etching, in comparison to the four source films. Both results would tend to reduce the total heterojunction area for cells formed in single source films and give higher open circuit voltage.

The importance of accurate, reproducible monitoring of substrate temperature during CdS deposition was highlighted during the program. Previously re-usable thermocouples were put in contact with the back foil surface using mechanical, lever-like arrangements. This method involved little disturbance to the substrate. Experiments on the program have shown that such thermocouples indicate temperatures 60 to 100°C higher than do units welded directly to the copper foil,

presumably due to a direct response to radiation from the substrate heater. Use of the welded thermocouples generally gave films with greater uniformity of grain size. Practical problems exist with the welded couples, however. The most serious are the possibility of shunting by the substrate material during the welding operation. Methods to avoid this are being explored.

A new method for revealing the CdS grain structure throughout the film thickness has been developed. This consists of weakening the specimen by etching away a thin stripe of the copper substrate foil, fracturing the CdS film in this weakened region, delineating grain boundaries by Cu_2S formation and removal, and SEM examination to correlate top surface and cross-sectional grain patterns. Future application of this technique should be useful in assessing the impact of process parameter variations on grain structure details relevant to cell performance.

Etching and Barrier Formation. Performance of finished cells is sensitive to certain aspects of the wet chemistry step. With processing involving normal transfers of the cells to the rinse beakers after HCl etching and after dipping in the Cu_2Cl_2 solution, open circuit voltage values were generally below 500 mV. At the termination of these wet processing steps, the cells are withdrawn from heated solutions. They retain on their surfaces liquid films of these solutions. During transfer to the rinse containers, the chemical concentration of the liquid films can increase due to evaporation of water, thus making the transfer interval a period of poorly controlled chemical reaction.

A flicking motion of the cells as they are withdrawn from the active solutions and then rinsed consistently results in cells with open circuit voltage in excess of 500 mV. This observation suggests that better control of the termination of the cuprous chloride barrier formation step is important for higher and more consistent cell performance.

An additional factor in the barrier formation step is the exclusion of air from the surface of the bath. Generally, this is done

by providing a blanket of argon under a loosely fitted cover plate. Such provisions are usually adequate at maintaining a cupric ion concentration in the bath low enough to prevent coloring of the solution. During sample withdrawal, however, more careful exclusion of air seems necessary. Improvements in V_{oc} and fill factor were associated with the use of a better fitting cover plate having a small window through which the cell was passed and sufficient argon flow to prevent easy entry of air through the window for the cell.

Gridding. No aspects of the use of standard evaporated gold grid electrodes were found to be critical for cell performance. The use of 2.5 μ m thick gold for the electrode grid does impose a high material cost, even for research purposes, considering that only 10% of the gold deposited on the cell surface is actually retained and used. Future work on lower cost metallization methods is recommended to alleviate this problem and its more serious longer term implications projecting commercial applications of Cu_2S/CdS cells.

Heat Treatment. A number of refinements were required before the hydrogen atmosphere heat treatment consistently produced high performance cells. It is important to eliminate occasions for long term (> 5 minute) exposure of the Cu_2S/CdS structure to high temperature (> 100°C) in the presence of air or surface adsorbed moisture. The latter effect can be minimized by keeping the cells in flowing hydrogen ambients for at least 30 minutes at room temperature before and after high temperature exposure. Without such precautions, cell performance results fluctuated during a sequence of overnight hydrogen heat treatments, probably reflecting changes associated with day to day variations in relative humidity.

Overview. A cell fabrication process incorporating special provisions for the critical factors discussed above can now be defined to serve as a baseline for future investigations. These can be undertaken for a number of purposes, among them: to improve cell performance per se; to upgrade selected processing steps, such as replacing gold in electrode gridding; to assess and improve the reproducibility of process

steps, e.g. the wet chemistry steps, in terms of cell performance parameters; to explore modified cell approaches for higher performance, e.g. the replacement of CdS by (CdZn)S; and to provide a more uniform population of cells for stability and reliability assessment.

2. INTRODUCTION

2.1 Objective

The objective of this program is to produce copper sulfide/cadmium sulfide solar cells with conversion efficiency of 9% or greater. Specifically, effort is to be applied to duplicate the basic elements of the cell fabrication sequence used at the Institute of Energy Conversion (IEC) of the University of Delaware to obtain 1 cm^2 cells of 9.15% efficiency.⁽¹⁾ This will demonstrate the transferability of process steps required for such cells.

2.2 Background

In earlier work at Westinghouse, the Clevite wet-processing method was used to produce 4 cm^2 cells with maximum conversion efficiency of about 6.3%.⁽²⁾ The process used by IEC was generally similar, but on careful analysis, was found to differ in some important details. Specifically, in the IEC process, cadmium sulfide powder is thermally evaporated from a single graphite crucible. In the Westinghouse process, four identical quartz sources were used to allow greater thickness uniformity of the CdS deposit over a large area. Scanning Electron Microscope (SEM) studies of the topology of Cu_2S penetration into CdS films prepared by the two methods show characteristic differences. In the four source films, conventional processing (a texturing etch in HCl and barrier formation by immersion in CuCl_2 solution) results in heavy pitting of the CdS film and very deep Cu_2S penetration along grain boundaries. For films produced by the single source method etch pitting is much less and the depth of Cu_2S penetration appears to be much less.* The latter is consistent with higher open circuit voltage due to lower

*cf. Fig. 4 in Ref. 1.

total diode opposing current from a smaller effective barrier area than that produced in the four source films.

In addition, the IEC process avoids high temperature air exposure of the cells after barrier formation. Instead, a sequence of annealing periods in a reducing ambient (containing CO or H₂) is used to form the Cu₂S/CdS barrier region. In the previous Westinghouse approach, a short high temperature (240°C) treatment in an air oven has been used.

Finally, the IEC cells have been made with evaporated gold grid electrodes contacting the Cu₂S layer (applied before the series of optimizing reduction anneal steps). An organic dielectric insulating film is applied to the cell surface prior to gridding to isolate the current collecting bus bar which is evaporated across the grid electrode fingers from the underlying Cu₂S layer. In the Westinghouse cells, a gold plated fine wire mesh was pressed against the cell surface for testing purposes. The nominal area of this contact was somewhat larger than that used by IEC.

2.3 Approach

The differences between IEC and Westinghouse cell fabrication details were judged to have first and second order influences on performance. Matters considered of most importance were the CdS film deposition method and its effect on grain size and the barrier interface topology, barrier formation and heat treatment details, and electrode grid contact preparation. Matters of second order importance were use of small area (1 cm²) cells, the role played by optical reflection of the back contact, consequences of spectral content of illumination, and cell packaging. These considerations were used in defining the tasks described below.

Prior to the start of the contract, Westinghouse personnel visited at IEC to observe details of CdS film preparation and cell processing. This first hand information was used to supplement the

process descriptions given in Ref. 1, and served to guide the definition of program tasks described below.

During the course of the program, two exchange visits were made, one at Westinghouse and one at IEC, to review in fine detail the cell fabrication practices of both groups. These served to identify subtle but potentially important differences in processing by the two groups. In addition to the information obtained by visits and observation of processing details, CdS film specimens and completed cells were exchanged to assess directly the differences in wet processing and annealing at the two facilities.

2.4 Program Tasks

The program effort dealing with processing and fabrication of cells of 9% conversion efficiency was planned with five tasks:

Task 1. Implement single source CdS evaporation and characterize effects on grain size and barrier topology.

Task 2. Implement details of IEC barrier formation regarding wet processing and heat treatments.

Task 3. Implement evaporated gold grid electrode contacts using IEC designs for aperture masks on 1 cm^2 cells.

Task 4. Assess spectral sensitivity of cells with regard to details of Cu_2S formation, barrier heat treatment and back contact reflectivity.

Task 5. Prepare, evaluate and package demonstration cells.

3. EVOLUTION OF CdS DEPOSITION AND FABRICATION STEPS

This section gives an outline of the changes made in the course of one year to improve the performance of $\text{Cu}_2\text{S}/\text{CdS}$ cells in which the Cu_2S layer is formed by wet chemical processing.

Prior to the start of the current program, Westinghouse processing of thin film $\text{Cu}_2\text{S}/\text{CdS}$ solar cells followed the methods originally developed at Clevite. A short description of the earlier Westinghouse process details given in Ref. 2 is repeated as Appendix A. On the basis of the details given in Appendix A of Ref. 1 and of a visit made to IEC, new processing procedures were instituted at the beginning of the program. Midway through the program an information exchange between IEC and Westinghouse was conducted. Its purposes were to identify specific differences between the cell processing details at both facilities, to evaluate the criticality of the differences and to generate a set of process modifications, as described in Section 3.2, for cell processing in the remainder of the program. A second information exchange was held after several months had elapsed, to "fine-tune" the cell processing in terms of subtle details of the type which often escape documentation. The outcome of that exercise is treated in Section 3.3.

3.1 Status at Beginning of Program

3.1.1 Substrate Preparation and CdS Deposition

Substrate preparation continued to emphasize cathodic degreasing and etching in nitric acid (See Appendix A) to avoid occasional occurrences of poor adhesion of the zinc plating and the CdS films. The CdS source material for evaporation had been previously sintered and reground.

For the CdS evaporation, graphite crucibles and the associated source heaters were ordered from the University of Delaware early in the contract period. Delivery of the graphite crucibles was made quickly, but the source heaters needed for use of these crucibles were not received during the first quarter. In lieu thereof, graphite crucibles capable of being used in the source heaters available at Westinghouse were designed, fabricated and evaluated.

Figure 1 shows the crucible design which was evaluated. The crucible had an integral collimation cone above the orifice. This section of the crucible extended above the surrounding source heater and required a separate cylindrical heat shield to prevent excessive heat loss from the extended crucible. The bottom loading feature of this crucible was advantageous in several ways: no space was required between the CdS charge and the quartz wool plug in the orifice — hence, more CdS could be charged, the quartz wool could be used repeatedly since it was undisturbed between runs, and finally there was no CdS residue to interfere with the bottom plug.

To obtain CdS films of adequate thickness for cell fabrication, a distance of 19 cm (7-1/2") was chosen, and efforts were made to pack more CdS into the graphite crucible. By careful tamping, a total weight of 13.0 grams of CdS could be changed into the graphite crucible, as compared to 11.5 grams without tamping. (The quartz crucibles previously used would hold up to 14 grams.) Under these conditions, the CdS film at the center of the film area was 28.7 μm thick, and at the corners of the 7.6 cm x 7.6 cm (3" x 3") specimen area it was 20.3 μm thick. Figure 2 shows the equal thickness contour lines measured for a typical CdS film deposited under these conditions using a substrate temperature of 220°C and a total deposition time of 17 minutes to empty the source.

For the CdS depositions, the substrate and the main evaporation heaters were powered simultaneously after the vacuum chamber was reduced to the range of 3.3 to 6.7 Pa. For the substrate, the intent was to bring its temperature to the desired value of 220°C as quickly as possible. This usually required 5 or 6 minutes. In the case of the CdS source

Evaporation Crucible-Material Graphite, DFP-3-2

All Dimensions are in Centimeters (inches) .

Cylindrical - O. D. 1.70 ± 0.005 ($0.67 \pm .002$)

I. D. 1.22 ± 0.013 ($0.480 \pm .005$)

Orifice - Dia. 0.32 to 0.33 (0.125 to 0.130)

Length 0.25 to 0.30 (0.100 to 0.120)

$22\ 1/2^\circ$ Conical Top Opening to Knife Edge Rim

45° Conical Taper
Inside

Bottom Piece
Threaded to Give
Close Fit to Bottom
of Upper Piece

9.4 Threads/cm
(24 Threads/in.)

Fig. 1. Design of cylindrical graphite evaporation crucible

Fig. 2. Thickness contours for a CdS film deposited using a single source of the type shown in Fig. 12.

heater, the source power was increased incrementally over a 16 min period to about 850°C, just below the temperature at which evaporation becomes significant.

A 4 minute period of glow discharge cleaning of the substrate was done, with the chamber pressure in the range of 3.3 to 10.0 Pa, maintained by cracking the main vacuum valve for short intervals. The main vacuum valve was then opened, the glow discharge terminated, the evaporation source power was increased to a predetermined nominal value for the desired rate of evaporation, and the substrate exposed to the CdS flux. Small adjustments of the source heater power were made to maintain a selected instantaneous rate as indicated by a quartz crystal rate monitor. Depositions were terminated at the desired film thickness indicated by the rate monitor.

3.1.2 Wet Processing

CdS films of the desired size were cut and taped to copper plates using Kapton® and electroplater's tapes. They were then etched in a 55% (by volume) hydrochloric acid solution at 60°C for ~ 2 seconds.* After rinsing in deionized water for ~ 1 second in the case of a flowing rinse or by dipping for about 1 second into each of two beakers of deionized water, the cells were immersed in the barrier forming solution.

To prepare the barrier forming solution (containing 6 gm of CuCl_2 and 2 gm of NaCl per liter) deionized water was boiled for 10 minutes under a flowing blanket of argon to remove air, and NaCl was added. The cuprous chloride was rinsed with 10% HCl to extract cupric ions, rinsed with acetone, dried using a Buchner funnel, and weighed. It was then added to the boiling solution, whose pH was adjusted to the range 2-3.5 with HCl .

Barrier formation involved a ~ 10 second immersion in the solution of the CdS film taped to its copper carrier plate. This was followed by successive rinsing in three beakers of deionized water and a

*This is the procedure described in Appendix A of Ref. 1.

final cascade rinse, all for about 1 second each. The cell was then dried with an argon jet.

3.1.3 Gridding and Heat Treatment

After the wet processing steps just described, the CdS film with the Cu₂S layer was provided with an organic insulator pad in the regions intended to accommodate the bus bar contact for the grid electrode. The insulator pad was produced by laminating a strip of an epoxy film material (ECC-038)* to the Cu₂S surface. The lamination was done in two stages: the first was for 30 minutes at 125°C in air, after which the protective sheet on the unbonded film surface was removed; the second was for 30 minutes at 180°C in air.

Prior to grid metallization the cell was annealed in a 50 cc/min flowing atmosphere of 6% H₂ in argon for 16 hours at 170°C. A double set of aperture masks, designed by the IEC group and purchased from Towne Laboratories, Inc. of Sommerville, NJ, was used to provide gold grid electrodes. The mask design is for 31 hours/cm (80 lines/inch) of 12.5 µm (0.5 mil) width. Gold was thermally evaporated for the grids at a rate of 1.5 to 2.0 nm/s to a thickness of 2 to 3 µm. At this stage, the cells were trimmed by shearing, and bus bars were applied. To avoid another vacuum deposition, these were formed using silver paint cured for 30 minutes at room temperature or by applying Eccobond V-91 silver-filled epoxy which was air dried and cured under house vacuum for 16 hours.

Heat treatment of the completed cells was done in a flowing (50 cc/min) 6% H₂/Ar ambient, using a tube furnace arrangement. The main tube was 5 cm in diameter and ~50 cm long. At the exhaust end the diameter was reduced to 0.5 cm to accept a Teflon® fitting for a line to the exhaust stack. A ground joint at the input end provided access for loading cell samples. Overnight anneals were done at temperatures of

*Supplier: Fortin Laminating Corp., 1323 Truman Street, San Francisco, CA 91341.

about 150 to 160°C. The cells were tested and subjected to additional annealing, as required to establish trends in performance.

3.2 Modifications

During the first part of this program a bottom-loading graphite crucible was used for the CdS depositions since it could be accommodated by the existing source heaters. Cells fabricated on these CdS films by the methods described in Section 3.2 gave lower photovoltaic performance results than were achieved earlier and reported in Ref. 2. Heaters were procured to allow use of the graphite source purchased from IEC. Figure 3 gives a comparison of the two sources. Further reduction of differences between Westinghouse and IEC cell processing resulted from a meeting held at Westinghouse. The modifications discussed below were considered to be important for achieving good cell performance.

3.2.1 Substrate Preparation and CdS Deposition

Nitric acid etching of the copper substrates prior to zinc plating was discontinued on the grounds that this could texture the electroformed copper and introduce undesirable variability for the CdS deposition. IEC practice of anodic cleaning in a commercial bath and of storing in a 40% sulfuric acid solution for at least 24 hours to remove oxides was instituted.

Changes in the CdS deposition methods were made to reduce the possibility of substrate oxidation and to improve reproducibility of source and substrate temperatures during deposition. For the latter purpose, a thermocouple was welded to the zinc-plated substrate instead of being held in mechanical contact using a more convenient lever arrangement as was done earlier. Experiments showed that the latter method gave thermocouple readings 60 to 100°C lower than in the welded case. The implications of this for CdS film structure are discussed in Section 4.1. A thermocouple, inserted in a monitoring well of the graphite source, was also used to verify that a predetermined schedule

Dwg. 7733A55

Graphite evaporation sources

Univ. of Delaware
Model
(Top Loading)

Westinghouse
Model
(Bottom Loading)

1 cm

Fig. 3. Cross-sectional views of cylindrical graphite crucibles of IEC and of Westinghouse design.

of changes in source power settings would produce an acceptable source temperature transient to begin a short (5 minute) sintering phase at 800 to 850°C.

To minimize oxidation of the substrate, a number of changes were made to earlier practice. First, glow/discharge cleaning of the substrate was discontinued. Previously, the moderate pressure needed for the discharge was maintained by deliberately leaking air into the system. Furthermore, no substrate or source heating was initiated until chamber vacuum was below 1.3×10^{-3} Pa (10^{-5} T). Finally, schedules for increased power settings to the source and substrate heaters were chosen, based on the specifics for the apparatus being used, to allow for the transient substrate temperature (nominally 220°C) to be reached at the end of the source sintering phase. At this point the substrate would be exposed to collect CdS as the source temperature climbed to its deposition value (1000 to 1100°C) in response to a final, predetermined step increase in source heater power.

3.2.2 Etching and Barrier Formation

Several cell processing modifications had been made at IEC since the period of the work reported in Ref. 1. These changes were incorporated in the work on this program in order to improve the reproducibility of result. One change was to apply TPA-85,* an epoxy-like adhesive, by screen printing methods to form the contact isolation pad prior to wet processing. In this way, curing of the material could be done prior to barrier formation. The dielectric was applied using a frame pattern, thus providing delineation of the area for the barrier. Curing of the TPA-85 can be done in a hydrogen atmosphere.

A second change in processing was to use a very mild etch solution of HCl (25% by volume) for 20 to 40 seconds prior to barrier formation. As will be shown in Section 4.2, this etch produces less

*Available from American Liquid Crystal Chemical Corp., Kent, OH 44240.

attack of the CdS surface than does the etch of Ref. 1 (55% by volume of HCl).

As regards barrier formation in cuprous chloride solution, only a slight modification to the earlier procedure was made, providing a slightly acidic bath for the Cu_2Cl_2 addition, with final adjustment of the pH to the range 2-2.5.

3.2.3 Gridding and Heat Treatment

The use of silver-containing paint and epoxy for the grid contact bus was discontinued to remove the possibility of silver migration during annealing, which might degrade cell performance. Instead, a second gold evaporation was to be done using an aperture mask to define the gold contact bus over the ends of the fine grid lines already deposited on the cell surface.

Several changes were made in details of the post-gridding heat treatments, primarily to reduce the possibility of exposing the cells to air while at high temperature. New quartz annealing ampoules were made; these had one end closed and the other fitted with a flat flange, grooved to accept an O-ring. A flat stainless steel plate, with fittings for gas input and exhaust and for a thermocouple well, sealed against the O-ring. The joint was secured with a clamp.

At the beginning of the annealing cycle the sealed tub with its cells was flushed with H_2/Ar for at least 30 minutes before insertion into the tube furnace. A similar cool-down period at the end of the anneal was used to prevent exposure of heated cells to the oxygen- and moisture-containing laboratory environment.

3.3 Refinements

With the use of modified processing conditions just described in Section 3.2.2, the photovoltaic performance of cells was improved considerably in terms of short-circuit current density and open-circuit voltage. Fill factor values were low, generally about 0.65. Furthermore,

cells fabricated on CdS film specimens supplied by IEC did not meet the performance levels reported by IEC for the same material. A thorough check of the documented processing details, e.g. in terms of suppliers of chemicals and the purity of the water used, did not reveal any obvious deviations from IEC practice at the time. Consequently, a visit was made to IEC to observe actual cell processing on films of CdS deposited at Westinghouse and at IEC. In this way it was possible to identify several aspects of cell processing not covered in written specifications.

Three important factors were identified and incorporated in the cell processing work of the fourth quarter of this program. Two factors are associated with the Cu_2Cl_2 wet process step of barrier formation. First, a complete argon blanket must be provided for the surface of the Cu_2Cl_2 solution. This is best done by having a close-fitting cover with a small slot through which the CdS film specimens are inserted. A strong flow of argon through a tube passing through the cover is vented through the specimen slot. The second factor is quick removal of the Cu_2Cl_2 solution from the specimen surface after dipping. To date, the best method is to impart a flicking motion to the specimen as it is withdrawn from the solution with rapid transfer to the rinsing operation.

Finally, the most consistent performance results were produced by heat treatments in pure, rather than diluted, hydrogen. This change requires some attention to safety matters. It is desirable to flush the sealed ampoule with nitrogen before introducing hydrogen if burning of the latter is to be done. This guarantees against the presence of an explosive mixture of H_2 and oxygen within the ampoule, tubing or the boil bubbler used to burn-off the hydrogen.

As a final refinement in cell fabrication, IEC workers suggested that detergent washing of the specimens be done prior to application of the TPA-85 coating and prior to etching. Such masking was considered to improve the adhesion of the dielectric material and to improve the uniformity of the wet chemistry operations. Washing

was done in a 60°C solution containing 1 ml of Micro^{*} detergent per 1 l of water. After rinsing in warm deionized water, the specimens were blown dry and checked to be free from stains.

Results of the various changes in CdS preparation and cell processing, as described above, are presented in Section 4. Some issues are not yet completely resolved, particularly as regards obtaining highly reproducible conditions and results. These are addressed in the recommendations of Section 5.

^{*}Available from International Products Corp., P.O. Box 118, Trenton 1, NJ.

4. RESULTS AND DISCUSSION

4.1 CdS Films

4.1.1 Film Structure Dependence on Evaporation Source Details

The structure of CdS layers deposited by single source evaporation shows major differences in comparison with that of films produced by multiple source evaporation, as was previously the practice at Westinghouse. These differences have a strong effect on the morphology of the subsequently formed Cu_2S layer and in the electrical properties of the finished cell. A major difference can be observed in terms of the effect of etching in HCl .

Figure 4 shows differences in the etch pitting of single (4a) and four source (4b) films produced by a 7 second etch in a 67% (by volume) of HCl in water at 45°C . Both films had been processed to form a Cu_2S layer which was subsequently etched in KCN to reveal grain boundary structure. The greater density and large size of etch pits in the film produced by the four source method is very evident.

In order to permit visualization of differences in the topology of the $\text{Cu}_2\text{S}/\text{CdS}$ interface in the two types of films, replicas were produced by applying an appropriate organic medium to surfaces of the type shown in Fig. 4.* The CdS films were then etched away and the replicated surfaces were examined in the SEM, giving the results shown in Fig. 5. It is evident from these views that in addition to the decreased density of etch pits in the single source film cells, the etch pits are not as deep and the penetration of the Cu_2S into the grain boundaries is also much shallower. We take this difference to be a fundamental one between films prepared by single source and multi-grain methods.

*The method for preparing replicas is discussed on p. 67 of Ref. 2.

(a)

(b)

Fig. 4. SEM comparisons of etch pit and Cu_2S penetration patterns in CdS films produced using (a) a single, and (b) a four evaporation source arrangement. (Beam incidence angle: 0° .)

(a)

(b)

Fig. 5. SEM views of replicas of the $\text{Cu}_2\text{S}/\text{CdS}$ interface on cells produced using (a) single, and (b) four source evaporation arrangements.

A model has been formulated to account for the differences between evaporated CdS films of single- and multi-source origin. For single-source depositions, at each point on the substrate, the preferred direction of growth is along the c-axis. This causes the c-axis of the crystallite at that point to be oriented toward the source.⁽³⁾ Experiments have been made at Westinghouse in which, for one deposition, the angle of the line from the substrate surface points to the source orifice was varied from 90° (directly over the source) to about 50°. The orientation of the crystallites for the latter case was well off the perpendicular to the substrate surface as revealed by SEM studies after Cu₂S formation and removal.

For any source of the type used on this program, the instantaneous rate of CdS evolution will fluctuate with time due to variations in source input power and in the configuration of the CdS charge within the source. For a single source evaporation this should have no effect other than to modulate properties of the growing CdS film which are sensitive to the arrival rate of the evaporant.

In the case of multi-source evaporation there should be a preferred direction of crystallite growth for each point on the substrate surface which is instantaneously determined by the source-substrate geometry and the instantaneous evolution rate of each sensor. Thus, the dominant source for a short time interval will cause favoring of a particular direction of growth at each point on the substrate. As the source evolution rate fluctuations cause another source to dominate, the preferred directions will shift. It seems likely then that a film produced using multiple sources, as was the earlier Westinghouse practice with four-source, will have sets of defects associated with the fluctuations in preferred directionality of the crystallites. These sets of defects should be absent for a film produced using a single source.

We hypothesize that the defects associated with fluctuations in the preferred growth direction of CdS crystallites cause the high density of etch pits in films grown with the multi-source method

(evident in Fig. 4b) in comparison with the single-source film results in Fig. 4a.

4.1.2 Influence of Substrate Temperature Control

During the first half of this program, the CdS films exhibited a strong tendency towards bimodality of the grain size distribution as delineated by using the Cu_2S penetration method. That is, such films showed a number of large grains with a much larger number of very small grains, as illustrated in Fig. 6. The film was dipped in concentrated Cu_2Cl_2 solution at 100°C for 6 seconds, and the Cu_2S so formed was removed by etching in KCN. The bimodal grain size distribution was not affected significantly by use of the graphite source purchased from IEC. No substantial difference in the grain size or structure of deposited CdS films could be attributed to this source, in comparison to the graphite source of Westinghouse design which was used previously. Additionally, no direct effect on cell performance was noted when in-situ glow discharge cleaning of the foil substrates was eliminated prior to CdS deposition.

The use of a thermocouple welded to the copper foil substrate for monitoring and controlling its temperature had a significant impact on results of the deposition. Previously, a mechanically contacted thermocouple applied to the back of the substrate was used for controlling power to a radiant heater positioned above the substrate. Several experiments were made using two thermocouples, one welded to the other, mechanically contacting the back of the foil substrate. Data taken simultaneously from both sensors showed that the mechanically contacted unit read higher than the welded one by 60° to 100°C . This difference is attributed to a high thermal contact resistance between the mechanically mounted couple and the substrate which makes that couple more responsive to radiant heating. Such an effect would result in control of the substrate heater power to produce a lower temperature in the substrate foil than indicated by the thermocouple.

CdS Film C-90

Fig. 6. Cu_2S penetration pattern of a CdS film illustrating bimodal grain size distribution revealed after formation and removal of a Cu_2S layer on an unetched CdS film.

The conclusion drawn from comparing results of the two methods of thermocouple attachment was substantiated when a welded thermocouple was used for substrate temperature control during actual CdS film depositions. In the first such use of the welded thermocouple, an indicated substrate temperature of 182°C was maintained at approximately the same substrate heater power previously used for depositions with the mechanically contacted couple indicating 220°C. The smallest grains in the resulting film were somewhat larger (Fig. 7a) than in the case with a mechanically contacted couple reading 220°C (Fig. 7b), but the tendency to form a matrix of small grains between larger grains is evident.

Typical depositions made with a welded thermocouple reading 220°C resulted in the larger grains and more uniform size distribution of Figs. 8a and b. In depositions for which deliberately higher substrate temperatures (240°C) were called for by the welded couple, the CdS grains were slightly larger, as shown in Figs. 9a and b.

4.1.3 A New Method for CdS Structural Evaluation

In the two preceding subsections, we have dealt with structural aspects of the CdS film as revealed by top surface examination after Cu_2S formation and removal to delineate large angle grain boundaries in the film. With that approach, anomalies such as the bimodal grain size distribution can be detected but very little insight is provided into the attendant three dimensional grain structure.

Earlier at Westinghouse, cross-sectioning of a completed cell had been used in conjunction with subsequent HCl etching to remove CdS and to indicate structural detail by the remaining Cu_2S material.* That technique had a number of disadvantages. The tedious sample preparation method — which involved potting the specimen resin, grinding and then fine polishing the surface section — did not lend itself to rapid, general application. Furthermore, with this method

* cf. pp. 53, 58-62 in Ref. 2.

(a)

(b)

Fig. 7. Examples of grain size differences (revealed by Cu_2S decoration and removal) in CdS films deposited at (a) 182°C as indicated by a welded thermocouple (Film #664) and at (b) 220°C as indicated by a mechanically contacted thermocouple (Film #663).

(a)

(b)

Fig. 8. Large grains (a) and uniform grain size distribution (b) in a typical CdS film (#667) prepared at 220°C substrate temperature indicated by a thermocouple welded to the back (heated) foil surface.

(a)

(b)

Fig. 9. Example of increased grain size in a CdS film (#676) deposited at 240°C, as read on a thermocouple welded to the back surface of the substrate. (a) High magnification view of typical area. (b) Lower magnification view to illustrate grain size distribution.

there was concern that mechanical damage during sample preparation could obscure features of interest. Finally, it was not possible to gain a good appreciation for the CdS grain structure by viewing the remnant Cu_2S .

A method has been developed to prepare CdS films for cross-sectional viewing in the SEM. Preliminary examination of film 728 has yielded new insights into CdS grain morphology. Film 728 was chosen because it had scattered anomalies, of a type often seen in CdS films prepared for solar cells. A particularly high density of these features is shown in a top surface view of a specimen processed with Cu_2S to define grain boundaries (Fig. 10).

The new preparation method involved the following steps:

(1) masking all of the samples with wax except for a centered, narrow strip on the back of the copper substrate; (2) etching through the copper along this strip so that locally only CdS remained; (3) breaking the CdS film into two pieces by fracturing it along the etched strip; (4) removing the wax; (5) dipping the fractured specimen in Cu_2Cl_2 solution; and (6) etching in KCN to remove the Cu_2S that was formed in the previous step.

The SEM view of Fig. 11a was taken with the electron beam nearly perpendicular to the fracture plane in the CdS, with the underlying copper substrate appearing indistinct because of the etched stripe. In this view, the fracture plane appears to have passed through the centers of adjacent hillocks on the original copper substrate. The views of the CdS film in these regions look like cross-sections of domes. The CdS grains emanate from the hillocks of the copper substrate at right angles to the curved surfaces.

Figure 11b shows a higher magnification view of the same general area. This photograph was taken at an angle to permit viewing of the grain delineation pattern on top of the CdS surface. The large surface grains extend to the tops of the copper substrate hillocks, whereas the smaller grains appear to originate within the film in areas between hillocks on the substrate.

Fig. 10. SEM view of the top surface of CdS film #728 after Cu_2S delineation of grain boundaries showing anomalous (lighter appearing) structural features. Scale: Small white bar = 5 μm .

(a)

(b)

Fig. 11. SEM views of the cross-section of CdS film #728 after Cu_2S grain delineation. (a) Viewed $\sim$ normally to the plane of cross-section. Horizontal scale: Small bar = $5\ \mu\text{m}$. (b) Viewed at an angle to both the top and cross-sectioned surfaces. Horizontal scale: Small bar = $5\ \mu\text{m}$.

Some anomalous features in film #728 are shown in Fig. 12. The defects are quasi-spherical in appearance in top surface SEM views. However, the cross-sectional view shows them extending deep into the film. In Fig. 12a one such defect at the cross-section plane is designated by the arrow. Fig. 12b gives a magnified view of the indicated defect in Fig. 12a, showing the relationship of its top surface features to the structure deep in the film. In future work, it should be possible to compare three dimensional structural aspects of films with and without such anomalous features. If conditions of their origin are better understood it may be possible to minimize or eliminate their occurrence.

4.2 Solar Cells

4.2.1 Results with Early Processing Methods

During the course of this program, a number of factors were identified as important for preparing $\text{Cu}_2\text{S}/\text{CdS}$ cells of high performance. These have been discussed in Section 3. Since the identification and application of these important elements of cell fabrication evolved over a period of some months, initial cell performance results were relatively poor.

At the beginning of the program pairs of specimens of CdS films from the same deposition run were processed in two ways to separate effects of CdS film properties and effects of subsequent processing. Standard (referred to as Type D) processing, as described in Section 3.1, involved IEC methods with some modifications, as inferred from Ref. 1, and private communications with members of the IEC group. For comparison, some cell processing was also done according to earlier Westinghouse methods (referred to as Type W processing), as described in Appendix A and in Ref. 2. Several differences between the two types of processing were considered to be unimportant as regards the performance of the cells. These include slight differences in the etch concentrations and temperatures and the duration of the etches, in the duration of the Cu_2Cl_2 dip process, and in the method of accomplishing the electrode

(a)

(b)

Fig. 12. SEM views of a portion of film #728 having growth anomalies present. (a) General view. Scale: Small bar = 5 μm . (b) Magnified view of the anomaly indicated by the arrow in (a). Horizontal Scale: Small bar $\approx$ 5 μm .

contact to the Cu_2S layers. We consider the major difference to have been the cell heat treatment after $\text{Cu}_2\text{C}_2\text{O}_2$ dip step.

With the standard process, heat treatments of relatively long duration were used and no special precautions were taken to remove surface adsorbed moisture prior to any of the high temperature exposures. As discussed in Section 3.1.3, the Cu_2S layer was exposed to half hour periods at 125°C and at 180°C in air as a part of the step in laminating the dielectric film for the electrode contact pad. In addition a 16 hr, 170°C anneal in flowing 6% H_2/Ar was done prior to grid metal evaporation. Each of these steps and any of the subsequent heat treatments in 6% H_2/Ar provided opportunities for moisture adsorbed on the cell surfaces to interact with the Cu_2S and the underlying material. In later refinements, these conditions were eliminated.

The alternative Westinghouse process involved one high temperature air exposure, nominally at 250°C . This was done between the $\text{Cu}_2\text{C}_2\text{O}_2$ dip step and the evaluation step using a pressed grid contact. This exposure, however, was of very short duration (~ 2 min).

Under the conditions just described, typical J_{sc} and V_{oc} results for the two types of processing on a single CdS film prepared by the four-source method are given in Table I. Values of short circuit current density were substantially higher with Type W processing. Fill factor values were low (< 0.55) for all the cells. Several cells were annealed in flowing 6% H_2/Ar , but no special precautions to remove surface adsorbed water were taken prior to the high temperature exposure. The data of Tables II and III show that short circuit current of the cells decreased during the heat treatment, suggesting a mechanism involving moisture or oxygen degradation of the cells. Such degradation in J_{sc} is typical of unprotected cells during long periods of storage.

Some improvement in the performance of cells prepared by Type D processing were realized by eliminating the air exposure during

Table I

Characteristics of 1 cm^2 Cells Made by Type D and by Type W Processing Prior to Post Gridding Heat Treatments.

(a) Type D Processing *

<u>Cell No.</u>	<u>V_{oc} (V)</u>	<u>J_{sc} (mA/cm²)</u>
599-5-A	0.400	1.4
599-5-B	0.405	4.0
599-5-C	0.400	4.5
599-5-D	0.405	5.3

(b) Type W Processing *

<u>Cell No.</u>	<u>V_{oc} (V)</u>	<u>J_{sc} (mA/cm²)</u>
599-7-A	0.428	10.0
599-7-B	0.425	9.5
599-7-C	0.428	7.6
599-7-D	0.430	9.8

* Processing types are described on p. 34.

Table II. Changes in Photovoltaic Characteristics of Two Typical Cells, Prepared Using Type D Processing, as a Function of Total Anneal Time at 170°C in Flowing 6% H₂/Ar

Cell No.	Total Anneal Time (hr)	V _{oc} (v)	J _{sc} (mA/cm ²)
599-5-B	0	0.405	4.0
	7.25	0.430	1.55
	17.5	0.425	1.56
	33.0	0.488	0.25
599-5-D	0	0.405	5.3
	17	0.440	2.2
	33	0.395	0.39

Table III. Changes in Photovoltaic Behavior of a Typical Cell (599-7-A) Prepared by Type W Processing, as a Function of Total Anneal Time at 170°C in Flowing 6% H₂/Ar

Total Anneal Time (hr)	V _{oc} (v)	J _{sc} (mA/cm ²)
0	0.428	10.0
3.5	0.435	6.1
11.0	0.445	6.0
18.0	0.440	6.4
23.0	0.435	5.1

lamination of the dielectric film for the electrode contact pad. A 6% H_2/Ar atmosphere was used for this step. Table IV gives results for two cells fabricated using a CdS film prepared by single source deposition methods. One of the cells was prepared over an area of the CdS film deposited over a thin ($\sim 0.3 \mu m$) zinc plating on the copper foil substrate, the other over a thick ($3.0 \mu m$) zinc plating. Each cell was first tested using a pressed grid electrode just after a 16 hr, $170^\circ C$ anneal in 6% H_2/Ar . Gold grid electrodes were evaporated on the cells and they were retested, without additional annealing.

The results of Table IV shows slight improvement in J_{sc} and fill factor values with the evaporated grids. This probably results from better contact to the Cu_2S layer near the edge of the laminated dielectric pad. Without subsequent annealing, J_{sc} values decreased in a fashion similar to that described earlier. Cells fabricated single source CdS films deposited subsequently were poorer in performance. This was attributed primarily to the fact that CdS films with bimodal grain size distributions were produced. A number of modifications to the film preparation and type D processing steps were made in order to upgrade cell performance. Details of these changes are discussed above in Section 3.2.

Table IV. Performance Comparisons of Type D Processed Cells, with Pressed and Evaporated Grid Contacts, Using a Single Source CdS Film Evaporated in Run No. C-85.				
Zinc Thickness (μm)	0.3		3.0	
Grid Type P = pressed E = evaporated	P	E	P	E
Efficiency (%)	2.7	3.3	2.5	3.0
V_{oc} (V)	0.468	0.455	0.455	0.430
J_{sc} (mA/cm^2)	10.8	11.8	10.4	11.9
Fill Factor	0.53	0.62	0.53	0.59

4.2.2 Results with Improved Processing

The most striking effect of changes made to improve CdS film deposition, cell processing and heat treatment (which are discussed in detail in Section 3.2) was the elimination of performance degradation with annealing in the early part of the heat treatment cycle. This improvement was attributed to the greater care in removing surface moisture prior to exposing the Cu_2S layer to a high temperature for long periods of time. To accomplish this, the specimens were kept in ampoules with flowing 6% H_2/Ar for 30 to 60 minutes at room temperature prior to insertion of the ampoules into furnaces for the required heat treatments. A similar cool-down period under a hydrogen atmosphere was observed before exposing the cells to room ambient again. Another factor in improving control of the heat treatment ambients was the use of a better ampoule design (Section 3.2.3), which reduced the possibility of leaks. Figure 13 gives an example of the photovoltaic parameter behavior for a single cell during a schedule of heat treatments of more than 150 hours total duration.

Other aspects of cell performance, such as higher values of J_{sc} , V_{oc} and fill factor, undoubtedly benefited from improvements in other aspects of cell fabrication. Among these were elimination of the glow discharge cleaning step prior to initiation of CdS film deposition, better control of substrate temperature with a welded thermocouple, and less pitting of the CdS film by the use of a milder CdS etch preceding barrier formation.

Figures 14, 15 and 16 give short circuit current density,^{*} open circuit voltage,⁺ and fill factor data for cells from 19 different CdS film depositions. Considerations of the possible effects of CdS deposition condition variables on cell performance leads to the

^{*}Projected for 100 mW/cm^2 ELH illumination.

⁺As measured for 90 mW/cm^2 illumination.

Figure 13. Example of photovoltaic parameter behavior for Cell #689-1 during the course of ~ 170 hours of heat treatment @ $\sim 170^\circ\text{C}$ in 6% H₂/Ar.

Figure 14. Short circuit current density (projected for $100 \text{ mW}/\text{cm}^2$, ELH illumination) performance of solar cells produced by standard processing during the third quarter of this program.

Figure 15. Open circuit voltage (for 90 mW/cm², ELH illumination) performance of standard process solar cells during the third quarter of the program.

Figure 16. Fill factor results for standard process cells during the third quarter of the program. Points at 10% signify cells for which fill factor values were not calculated.

following observations:

- (1) The best cells with highest J_{sc} and V_{oc} values were made on films (671 and 681) prepared a month apart in time using pre-sintered CdS source material under similar conditions of substrate temperature (Table V gives typical cell measurement results).
- (2) Cells produced on films from intervening deposition runs had much lower values of J_{sc} with only moderate values of V_{oc} (ranging from 400 to 450 mV). The factor common to these cells was their fabrication from films produced from unsintered CdS source material.
- (3) The use of higher substrate temperatures (240° vs. 220°C in standard runs) in Runs 676 through 680, although it produced larger CdS grains in the deposited films, did not improve open circuit voltage.

Table V. Typical Parameters for 90 mW/cm ² ELH Illumination of 1 cm ² Cells from the Two Highest Performing Cell Lots				
Cell No.	V_{oc} (v)	J_{sc} (mA/cm ²)	ff	n (%)
671-5	0.480	17.50	0.66	5.61
-6	0.486	18.13	0.67	6.00
-8	0.485	18.13	0.69	6.16
-9	0.455	18.75	0.55	4.90
681-5	0.510	20.20	0.63	6.53
-6	0.490	19.50	0.65	6.39
-8	0.426	16.83	0.33	2.60

4.2.3 Impact of Processing Refinements

Improved cell performance was associated with the changes (Sections 3.2.2 and 3.2.3) which reduced the possibility of air or surface moisture degradation during long, high temperature heat treatment steps. In addition, improvements in CdS film deposition details (Section 3.2.1) had also been incorporated into cell processing. Even with these changes, the performance of cells fabricated using CdS specimens supplied by IEC was below that expected, particularly in terms of V_{oc} and fill factor values. A visit to IEC was made for the purpose of observing minute processing details, including such matters as operator movements which are not usually treated in process specifications.

A part of that interaction with the IEC group involved co-processing of CdS films from Westinghouse and from IEC by IEC personnel. Eight of the cells fabricated in this exercise were split into two groups: one for annealing and testing by Westinghouse; the other, by IEC. Each group contained two cells on IEC material and two on Westinghouse material. Data on peak efficiency, short-circuit current density (projected for 100 mW/cm^2 illumination), open circuit voltage and fill factor are given in Table VI. These results established that the CdS material prepared at Westinghouse was capable of making 7% cells with short circuit current density values (for 100 mW/cm^2 illumination) comparable to those obtained at IEC. Open circuit voltage and fill factor values for the cells on Westinghouse material were slightly poorer than for those using IEC films. The similarity of results irrespective of the facilities used for heat treatment established the adequacy of annealing procedures at Westinghouse.

In subsequent cell processing and treatment at Westinghouse three changes were made for greater consistency with IEC methods, as described in Section 3.3. These involved more careful exclusion of air from the surface of the Cu_2Cl_2 bath for the dipping step, more rapid removal and rinsing of the Cu_2Cl_2 solution from the cell surface after the dipping step, and use of undiluted hydrogen gas for the heat treatment steps. Results of incorporating these changes on photovoltaic performance

Table VI. Comparison of Westinghouse and IEC CdS Films and Annealing Procedures on Cells Produced Simultaneously at IEC

	Annealed and Tested at							
	Westinghouse				IEC			
CdS Film	η (%)	J_{sc} (mA/cm ²)	V_{oc} (mV)	Fill Factor	η (%)	J_{sc} (mA/cm ²)	V_{oc} (mV)	Fill Factor
(W)	7.3	20.4	510	0.63	7.4	21.5	511	0.68
# 681	7.1	20.1	490	0.65	6.6	21.7	505	0.62
IEC	8.4	20.4	525	0.71	6.8	18.1	522	0.72
#2-1115	8.4	20.0	523	0.72	6.7	18.1	520	0.72

are shown in Figures 17 through 20 for 106 cells, processed over a period of about four months. In these examples, various photovoltaic performance parameters are shown as functions of the CdS film identification number. No data are shown for cells on films 676 through 681, since results on those films are included, in Figures 14 through 16. Films 682 through 697 exhibited strong evidence of bi-modal grain size distribution and they were excluded from cell fabrication. Also excluded were films 717 through 722, which were produced under experimental conditions to study substrate temperature control.

The most striking overall improvement during this period was the consistent achievement of open circuit voltage values of 500 mV or higher (Fig. 17) in 75% of the cells. There was considerable spread in the fill factor values (Fig. 18), and cells fabricated from films produced after #705 had values below 0.70. Values for J_{sc} (for 90 mW/cm² illumination) exhibited considerable spread in distribution as well, but there was no significant trend in the values associated with the CdS film number. Finally, the efficiency results (Fig. 20) exhibited a widely spread distribution, reflecting lack of strong correlation between J_{sc} and fill factor. The histogram of Fig. 21 suggests that most of the cells give results distributed about a mean efficiency value of 6 to 6.5%, with approximately 30 cells having abnormally poorer performance, below 4.5% in efficiency. Future effort, involving better control of the important aspects of CdS film preparation and cell fabrication which were identified by work on this program, should result in higher efficiency cells with smaller variations in performance parameters.

4.3 Automated Cell Testing and Data Handling

Cell testing has been automated with the addition of a Digital Equipment Corporation MINC computer system. This system was based on the LSI-11 computer, which was selected because of the ease of handling input and output analog signals. The system is configured as shown in Fig. 22.

Fig. 17. Distribution of open circuit voltage behavior on 106 cells fabricated from various CdS films over a period of four months.

Fig. 18. Fill factor behavior on 106 cells fabricated on various CdS films.

Fig. 19. Short circuit current density (for 90 mW/cm^2 illumination) for 106 cells fabricated over a four month period on various CdS film specimens.

Fig. 20. Scatter of conversion efficiency values for cells fabricated on CdS films produced over a four month period.

Fig. 21. Histogram showing distribution of conversion efficiency values for 106 cells fabricated over a four month period on various CdS film specimens.

Fig. 22. Schematic representation of automated cell testing and data handling.

The output from the D/A converter is sent to a Hewlett Packard amplifier. The voltage is sensed directly across the cell by one channel of the A/D converter while the current is measured using the voltage drop across a resistor. The system is programmed to sweep the voltage negative to positive extremes. The voltage sweep is controlled by the computer. The output from the D/A converter is stepped by an incremental amount and the voltage and current are monitored after each step. The size of the increment is varied over the sweep to yield a relatively smooth curve. The speed of the sweep is controlled by repeated sampling of the output after each increment. This averages the signal and also slows the sweep to the desired range. Presently the signal is sampled 50 times at each point to give a total sweep speed of approximately 11 seconds.

No processing is done during the sweep; the I-V data is stored as an array at the conclusion of the sweep and the raw data is stored as a file on a floppy disk. The data is also processed and the desired parameters, e.g. V_{oc} , J_{sc} , fill factor and efficiency are extracted. This manipulation is followed by a curve fitting routine developed at IEC to obtain the series and shunt resistance as well as the light generated current and the reverse saturation current for a simple equivalent circuit representation of the cell. These data are printed out on the line printer immediately to produce a hard copy output. They are also stored in a second file under the cell identification code.

The use of this second file, with the extracted parameters stored under the cell code, allows the computer to be used to generate plots on which Figs. 17 through 20 were based. Additional analysis of the data can also be performed. Presently, programs have been written to search the stored files and to order the cells in terms of photovoltaic parameters. This feature was used to provide data for the histogram of Fig. 21.

5. CONCLUSIONS AND RECOMMENDATIONS

General. Several key factors have been identified in the present fabrication procedures required to produce high efficiency $\text{Cu}_2\text{S}/\text{CdS}$ thin film solar cells. These are:

- Use of single evaporation sources for the CdS film evaporation,
- Control of substrate temperature with welded thermocouples;
- Elimination of deep etch pitting during texture etching of the CdS surface;
- Exclusion of air above the Cu_2Cl_2 during barrier formation;
- Rapid and thorough removal of Cu_2Cl_2 solution residues after barrier formation;
- Removal of surface adsorbed moisture and exclusion of air during high temperature hydrogen atmosphere heat treatments of cells.

The identification of these factors was aided by experience acquired at Westinghouse with this general approach for producing $\text{Cu}_2\text{S}/\text{CdS}$ solar cells. That background made it possible to contrast specific effects of procedures used at the Institute of Energy Conversion with effects of other processing methods.

Preparation of CdS Films. On this program, the most significant aspect of film preparation has been the use of a single graphite evaporation source instead of an arrangement of four quartz sources used previously. With all other preparative factors being the same, the single source method produces CdS films which have larger grain size and which develop fewer deep etch pits during texture etching. It

is hypothesized that fluctuations in the evaporant evolution rates among the four sources result in a more defective grain structure. Smaller grains and a high density of deep etch pits would increase the area of the $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction, causing higher values of diode opposing current and lower values of V_{oc} than in structures otherwise comparable, but with a smaller heterojunction area.

Another important element in CdS film preparation is accurate monitoring and control of the substrate temperature during deposition. Previously we had used thermocouples (TCs) held in contact with the back of the substrate by a lever arrangement. In experiments comparing these and TCs welded to the substrate, the former indicated temperatures from 60 to 100°C higher than the welded units, presumably by being more responsive to radiational heating. As a consequence, when the mechanically contacted TCs were used for substrate temperature control, as was the earlier practice, actual substrate temperatures could have been considerably lower than the desired 220°C. Introduction of welded TCs for substrate temperature monitoring was associated with elimination of severe bimodality in grain size distributions.

Some problems still exist with the use of welded thermocouples. In experiments using two welded TCs, there was occasionally substantial disagreement in the readings. This has been attributed to shorting of the the TC junction during welding. Effort should be applied to permit reliable attachment of TCs to the substrate while avoiding the possibility of shorting.

Development of a technique to define the grain structure in cross-sectional specimens of CdS films opens new possibilities for characterizing substrate and preparation parameter influences on grain features. This should help to resolve issues on optimum substrate preparation which have been raised, but not resolved, on this program. One such issue involves the advisability of using a nitric acid etch of the substrate prior to zinc plating, since effects of the resultant texturing are not currently appreciated.

Etching and Wet Processing of Barriers. The wet chemical treatment of CdS films and barriers involves heated solutions. On withdrawal from these solutions, the surfaces of the workpieces are covered with a liquid film which begins to evaporate. Potential exists for increased concentrations of chemical reactants in these films before they are rinsed, thus permitting an interval of poorly controlled chemical action.

Improvements in values of open circuit voltage and fill factor resulted when a sharp flicking action was used to remove some of the solutions retained on the cell surface prior to rinsing after these steps. A simultaneous corrective action was to blanket the Cu_2Cl_2 bath more effectively with an argon cover gas. This was done by increasing the gas flow rate into the space between the solution and a cover plate over the container and by providing only a small window in the cover for cell insertion and withdrawal. Better means should be sought to remove the film of solution from the cell surface as it is withdrawn from the Cu_2Cl_2 bath.

Gridding. The use of evaporated gold for grid contacts in the $\text{Cu}_2\text{S}/\text{CdS}$ cell has become very expensive, even for a research and development study, due to the large numbers of cell lots being processed. With the thermal evaporation method being used, approximately 0.6 Troy ounce of gold is required for each process lot (grids and bus bar).

Two routes are open to alleviate this problem. One might use a thin evaporated layer of gold, then selectively electroplate only the grid pattern to the required thickness. This had disadvantages in the additional chemical exposure of the active Cu_2S surface required for patterning and for removal of the unwanted portions of the initial thin gold layer. A second route is to abandon the use of gold entirely and use instead less costly metals. The latter approach appears to be preferable, although successful identification of an appropriate metal system must include concern for its implications on the long term reliability of cell operation.

Heat Treatment. Evolutionary improvement in cell performance on this program was associated with actions taken to minimize the possibility of air exposure or of retaining surface adsorbed moisture when cells were subjected to long (> 15 min) high temperature (> 100°C) treatments. These actions included use of hydrogen rather than air ambients for curing the dielectric layers used as insulation under the bus bars; use of a flange-sealed ampoule for hydrogen heat treatments; and holding cells in flowing hydrogen ambients within the ampoule at room temperature for at least 30 min before and after heat treatments.

Before any of these special precautions was taken, cell performance was poor initially and declined with subsequent heat treatments. This behavior suggests an air- or moisture-related degradation mechanism. When all but the last action had been instituted, cell performance was often erratic during the course of several heat treatments. This behavior may have reflected changing levels of humidity in the laboratory and variations in the time of cell exposure to the laboratory ambient.

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7. REFERENCES

1. John D. Meakin et al., "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research," Final Report: 7/1/77 - 8/31/78, Contract No. EG-77-C-03-1579, May 1979.
2. J. R. Szedon, F. A. Shirland, W. J. Biter, T. W. O'Keefe, J. A. Stoll, S. Fonash, "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research," Final Report: September 30, 1977 to July 31, 1979, Contract No. EG-77-C-03-1577.

APPENDIX A

MATERIAL PREPARATION AND CELL FABRICATION PROCEDURES PREVIOUSLY USED AT WESTINGHOUSE, CONSTITUTING TYPE W PROCESSING

A processing sequence of four principal steps was used for producing most of the thin film cells on this program: substrate preparation, CdS material preparation, CdS film deposition and Cu₂S barrier formation. No front surface electroding was done for large area cells since a pressed gold plated mesh screen was used as the front contact for cell evaluation. Pertinent details of the main fabrication steps, adapted from earlier work, are given below.

Substrate Preparation. Electroformed copper foil, 1 ounce gauge (.0014" nominal thickness) was used for standard processing. As supplied by the manufacturer,* the foil had a thin proprietary coating to inhibit oxidation. The substrate material was cleaned by cathodically degreasing using a commercial alkaline degreaser, followed by a light etch in warm (40-45°C) 1:3 HNO₃ solution. After water rinsing, a layer of zinc about 1 to 2 microns thick was deposited onto the copper surface by electroplating using a commercial fluoborate bath. After water rinsing and drying in absolute alcohol, the substrates were used immediately (within one hour) for CdS film deposition. The mat side of the foil was used for most CdS film depositions during this program.

CdS Material Preparation. A commercial luminescent phosphor grade of CdS powder was used as the starting material.⁺ The CdS material used in this program was given a light sintering - in vacuo to 850°C-- and then crushed using an alumina mortar and pestle to pass a 42 mesh screen, prior to charging into the evaporation sources.

*Gould, Inc., Foil Division, McConnellsville, Ohio.

⁺Type 118-8-2 Cadmium Sulfide Electronic Chemical, "Iron Free," as supplied by General Electric Co., Chemical Products, Cleveland, Ohio.

CdS Film Deposition. The CdS film depositions were accomplished by radiation heating of the CdS in the sources to cause evaporation upwards and growth on the substrate above. Quartz vials were used for the evaporation sources, with their necks lightly packed with quartz wool to prevent CdS particle spattering during film deposition. The temperature of the evaporation sources was in the range of 1200 to 1300°C and was regulated by controlling the power to the radiation heaters surrounding the sources. The substrate temperature, about 220 to 230°C, was monitored by a small thermocouple in pressure contact with the back surface of the substrate, used to control the power to a radiant heater above the substrate.

In this program, the substrate size was fixed at 7" x 7" with the outer 1/2" periphery not used for cells. For this substrate, size 4 sources were used and these were spaced at the corners of a 6" square. The source to substrate distance (about 8") was adjusted to yield thickness uniformity of the CdS film over the 36 in² of active area. The CdS film deposition rate was about 250Å/second and was adjusted by changing the power input to the source heaters. In a conventional 20 minute deposition period, the power to the sources is held constant. Sufficient CdS material was charged into the sources to prevent exhaustion during deposition and evaporation was stopped at the end of a period, usually 20 minutes, which had been found empirically to yield the desired CdS film thickness. Films of about 30 μm were produced for most of this program.

Pre-heating of the substrate and sources and glow discharge cleaning of the substrate were used. Specifically, the following sequence was followed:

1. Rough the chamber to 25×10^{-3} Torr and maintain pressure between 25 and 100×10^{-3} Torr until the main valve is opened.
2. Pre-heat the sources by gradually increasing the power to the source heaters over a 15 minute period to a level just below the point where noticeable vaporization of CdS will occur.

3. Pre-heat the substrate so that its temperature is stabilized at the desired operating temperature for several (3 to 5) minutes prior to the start of evaporation.
4. Use a plasma glow discharge to clean the substrate for 2 to 5 minutes just prior to the start of evaporation.
5. Open the main valve to the diffusion pump while simultaneously increasing source heater power to operating level.

Glow discharge cleaning was carried out at a power input level just below the point where sputtering of the electrode occurs. The glow discharge terminated automatically as the pressure in the chamber dropped when the main valve was opened. A high capacity pumping system and the use of a vacuum ballast tank made possible a rapid decrease in chamber pressure and thus a minimum interval--just a very few seconds--between the cut-off of the glow discharge plasma and the start of CdS deposition.

Cu₂S Barrier Formation. The barrier formation process consisted of HCl etching, dipping in CuCl solution, rinsing, drying and oven heat treating of the CdS film. The etch involved a 7 second immersion in 2:1 HCl solution at 45°C. The Cu₂S was formed by a 6 second immersion in concentrated CuCl solution at 100°C. Both of these steps were carried out with vigorous agitation of the work piece and/or the solutions, and with rapid transfer of the workpiece to the next operation. The chemical reaction was quenched and the solution drag-out removed by four de-ionized water rinses each of about 1 second duration. These were followed by drying in an argon gas stream. Heat treatment was a 2 minute soak in a circulating air oven set at 250°C. This treatment can be delayed for up to several hours without apparent deleterious effects.

Immediately after heat treatment, the photovoltaic performance of the cells was evaluated, using a gold-plated wire mesh (~ 15% coverage) pressed into place by a plastic block.