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CADMIUM SULFIDE/COPPER SULFIDE: HETEROJUNCTION
CELL RESEARCH

MASTER

Technical Progress Report No. 4 for July 1–September 30, 1978

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November 20, 1978

Work Performed Under Contract No. EG-77-C-03-1577

Westinghouse R&D Center
Pittsburgh, Pennsylvania

U.S. Department of Energy

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Solar Energy

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Westinghouse R&D Center
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CADMIUM SULFIDE/COPPER SULFIDE
HETEROJUNCTION CELL RESEARCH

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ABSTRACT

Important advances have been made in five technical areas during this quarter: topological investigations of film materials and cells, characterization of current transport and collection in $\text{Cu}_2\text{S}/\text{CdS}$ cells, preparation and application of small area film cells, correlation of photoresponse image and structural features in film cells and means of preparing $(\text{CdZn})\text{S}$ alloy films. The use of potassium cyanide etching of Cu_2S layers on polycrystalline CdS films defined areas 1 to 5 μm across with the latter covering 30 to 50% of the surfaces studied. Large grains may strongly reduce short circuit current levels. Laser scanned photocurrent response of tapered Cu_2S layers on single crystal CdS has been refined to directly treat photocurrent-transmission data, allowing more firm estimates of lifetime, surface recombination velocity and heterojunction collection efficiency. Delineation of small area film cells has been done successfully using photolithographic methods. As used, these methods have no deleterious influence on cell behavior. With arrays of small cells on a single substrate it was possible to establish that increased junction opposing current (lower V_{OC}) results from longer immersions in CuCl during Cu_2S formation. Patterns of high response in laser-scanned photocurrent images have been correlated with SEM images of grain boundary patterns. Difficulties in the use of a

quadrupole mass analyzer to monitor component fluxes during (ZnCd)S evaporation were isolated and overcome, allowing use of the method to prepare films for structural, electrical and cell evaluation.

1. SUMMARY

Important advances have been made in five technical areas during the fourth quarter of this program, viz.: (1) topological characterization of CdS films and of the interfacial region in $\text{Cu}_2\text{S}/\text{CdS}$ film structures; (2) refinements in Cu_2S minority carrier transport characterization for structures having Cu_2S films of tapering thickness; (3) preparation of small area thin film cells and their subsequent use to assess electrical uniformity and chemical processing influences on photovoltaic behavior; (4) correlation of features in laser scanned photocurrent response and scanning electron microscope images relating to grain boundaries in CdS thin films; (5) deposition of $(\text{ZnCd})\text{S}$ thin films.

An alternate method of examining the topography of the $\text{Cu}_2\text{S}/\text{CdS}$ interface was developed. This method consists of removing the Cu_2S layer from a cell by etching in potassium cyanide solution, applying a plastic replicating material to the remaining CdS surface, and then etching away the CdS layer. An analysis was made of the Cu_2S structural configurations of high and low current output cells. The higher current cells had deep Cu_2S penetration which may have been enhanced by the presence of pits produced by the pre-barrier etch.

A study was made of the topological consequences of CdS etching parameters, i.e. duration, temperature, and HCl concentration. New insights have been obtained into pitting and texturing of the CdS film surface, and into the influences of structure of the CdS film and topography of the metal foil substrate.

The use of KCN etching of Cu_2S layers formed on polycrystalline CdS films has revealed deep, steep-sided penetration of the Cu_2S , presumably along grain boundaries. The grains so defined vary in width from less than a micrometer to about 5 μm . It has generally been accepted that

1 μm grain sizes were typical. The coverage of a large fraction (~ 30 to 50%) of the film surface by grains considerably larger than 1 μm could result in reduction in short circuit current. The contribution was less with larger grains because of the favorable absorption and collection geometry presented by the edge-on junction at the boundaries of columnar grains. In this regard, considerable variations in grain size distributions over a single film and from run-to-run were observed. It is clear that conditions controlling grain size need to be better understood. Only the use of films with more uniform and reproducible grain size characteristics will permit achieving good cells by the wet CuCl immersion process.

During this quarter, the use of laser scanned, photocurrent response of a tapered Cu_2S layer on single crystal CdS has been refined. Data for photocurrent amplitude as a function of optical transmission can be obtained and interpreted directly. Theoretical treatments have also been extended to show more clearly the individual influences of minority carrier lifetime and surface recombination velocity on the photocurrent-transmission characteristic for tapered films. This work has provided the basis for more firmly estimating lifetime, surface recombination velocity and heterojunction collection efficiency for standard and heat aged specimens. Specifically, we found that short heat aging at 180°C does not significantly change minority carrier diffusion length, but may increase surface recombination velocity (from near zero) to about 10^4 cm/sec. In addition such heat aging reduces heterojunction collection efficiency from initial values near $\sim 75\%$ to less than 1%. As an extension of the work on single crystal CdS substrates, tapered Cu_2S layers formed on unetched polycrystalline CdS films have given photocurrent response signatures (as a function of position along the taper) qualitatively similar to those on single crystals. The convenience of treating data in terms of photocurrent-transmission curves is not yet possible. Means are required for removing the supporting metal substrate and relating light transmitted through the CdS to absorption in the Cu_2S layer.

Delineation of small area cells using thin film CdS substrates has been successful. Etch removal of the Cu_2S layer with mesas formed by Apiezon wax masking has been done successfully. This has allowed some insight into the role played by locally poor electrical performance in terms of cell behavior. In addition it has been possible to reduce the excessive reverse current in individual small area cells by hydrogen treatment. This treatment produced reverse current levels comparable to those for other cells on the same specimen whose initial reverse current was very low. Since wax masking and etching is a tedious method yielding mesas of non-uniform size, photolithographic methods were developed for forming large arrays of cells. Initial work was done to establish that the chemical and heating cycle influences required for photolithography with Shipley AZJ and Waycoat IC materials were not detrimental to cell performance. Two levels of processing were established. In one, patterned resist films on unetched or lightly etched CdS films were successfully used to delineate arrays of small area cells. Standard HCl etching of the CdS could not be used either before masking or after masking. A more sophisticated level of processing has been developed using a double layer mask: Waycoat IC over an evaporated SiO_2 layer. This permits both standard etching of CdS films in HCl and subsequent CuCl immersion in the open window areas.

With processing using a single photoresist masking layer, arrays of small cells were formed on individual CdS film specimens. Groups of cells on the same film were processed by varying CuCl immersion times by selectively masking with resist after successive exposures. The main result of this study was the detection of increased junction opposing current (hence lower V_{OC}) with increased CuCl exposure time. Cells formed on highly etched CdS films exhibited less sensitivity to CuCl immersion time in this regard.

Laser scanned photoresponse images on thin film cells using unetched CdS indicated patterns of high response similar to those produced by etch removal of Cu_2S films. With the availability of a cell corner as a reference, it was possible to obtain an SEM image of the

of the same region. This verified that most of the photocurrent response features correlate with Cu_2S delineated grain boundaries. Some topological features (fissures and minor surface irregularities) in the SEM images were not reflected in photocurrent features. This is the first time that a direct relationship between structural and photocurrent response features has been shown. The results also highlight the role of crystallite size in cell response.

Several difficulties were found in the use of a quadrupole mass analyzer (QMA) to monitor component fluxes during co-evaporation of ZnS and CdS to form alloy films of controlled composition. Means have been established to permit practical use of the QMA approach. Films of several compositions were produced on glass substrates and evaluated optically. The details of the approach for alloy film preparation and QMA monitoring are sufficiently well established to allow future use of the method for structural, electrical and cell evaluations.

2. INTRODUCTION

2.1 Objective

The objective of this program is to conduct research on solar cells of the copper sulfide/cadmium sulfide and copper sulfide/cadmium sulfide-zinc sulfide alloy) types with the goal of producing thin film cells capable of 10% AM1 conversion efficiency with less than 5% degradation in cell performance over a use period of 20 years.

2.2 Background

In the present program, the approach deals with three topics: (1) Control of selected Cu_2S and CdS material and physical properties relevant to solar cell operation, e.g., thickness, crystallite size and electrical characteristics and determination of effects of these properties on cell mechanisms and performance. (2) Production and evaluation of structures with simple geometries, usually on single crystal substrates. (3) Extension of significant results in the foregoing areas to thin film $\text{Cu}_2\text{S}/\text{CdS}$ or $\text{Cu}_2\text{S}/(\text{CdZn})\text{S}$ solar cells for a better understanding of the ultimate performance of such cells. The program planned to execute this work involves nine tasks. They are:

1. CdS preparation, evaluation and control.
2. Cu_2S preparation and evaluation.
3. Prototype cell fabrication and evaluation.
4. $\text{Cu}_2\text{S}/\text{Zn}_x\text{Cd}_{1-x}\text{S}$ studies.
5. Model development and refinement.
6. Copper migration, oxygen and heat effect studies.
7. Design, fabrication and evaluation of improved cells.
8. Assessment and extrapolation of program results.
9. Cell process cost analysis.

2.3 Emphasis for this Quarter

Methods developed earlier on the contract⁽¹⁾ for topological characterization of various aspects of thin film $\text{Cu}_2\text{S}/\text{CdS}$ structures have been extended, as described in Section 3.1. Application of selected methods to evaluate topological effects of controlled changes in etch procedure parameters of CdS is treated in Section 3.2. In Section 3.3 topological comparisons of CdS films deposited at temperatures from ~ 200 to 600°C are discussed.

Effort on the characterization of minority carrier transport in Cu_2S layers has continued. A refined method for such evaluation, eliminating the need to determine the thickness profile of tapered Cu_2S films, is described in Section 3.4. Also treated are effects of heat aging as determined by such measurements. Problems in application of the method to polycrystalline thin films are discussed. Consideration of bias light spectral content on the response of heat aged cells is described in Section 3.5.

Extensive use has been made of small area cells during this quarter. Several methods of delineating cell area have been established (Section 3.6). With the availability of arrays of small cells on a single film substrate it has been possible to study chemical influences in more detail than previously. Section 3.7 gives comparisons of photovoltaic behavior for unetched and etched CdS thin film cells for a range of CuCl immersion times during the Cu_2S layer formation. With small rectangular cells it has become possible to obtain high resolution (distinguishing features less than a micrometer in size) photocurrent and SEM images of the same part of a cell. The results of such comparisons are discussed (with emphasis on the role of Cu_2S penetration down grain boundaries) in Section 3.8.

In Section 3.9 (ZnCd)S evaporation effort is described. Problems associated with the quadrupole mass analyzer are discussed and results of optical properties for films of several compositions are given.

3. PROGRAM PROGRESS

3.1 Topographical Studies of Cu₂S/CdS Film Structures

3.1.1 Background

In the previous report⁽¹⁾ techniques were described for separating the Cu₂S layer from Cu₂S/CdS thin film solar cells by slowly dissolving away the CdS. Three types of specimens were prepared by this technique and examined in the SEM: free-standing, adhesively mounted, and cross-sectioned Cu₂S layers. The free-standing layers appeared to suffer some breakage during handling. Also, the depth of penetration of the Cu₂S into the CdS, and a useful statistical measure of the area and density of local Cu₂S penetrations could not be determined accurately. Adhesively mounted Cu₂S layers had less tendency towards breakage, but the epoxy adhesive used did not adhere well to the Cu₂S. As a result the Cu₂S layers tended to float away during the CdS dissolution unless some CdS was left in place. In that case there was some uncertainty in locating the boundary between the Cu₂S and the CdS layers. The cross-sectioning of potted samples, however, gave a good quantitative measure of some geometric details of the Cu₂S structure, though only a few specimens were studied in this way.

3.1.2 Potting and Cross-Sectioning

Because of the encouraging initial results with the potting and cross-sectioning method of Cu₂S layer characterization, additional work was done on it during this period. However, difficulties were encountered in repeating the earlier results. Several encapsulants were evaluated, but the chief difficulty seemed to be in the lapping and polishing operation after cross-sectioning. The composite structure of CdS film cells, which includes layers of varying hardness is difficult

to lap and polish to optical flatness, and this is further complicated by the tendency of CdS to cleave in the direction being lapped. Several different abrasive grit materials were tried, but the results were highly variable. More work needs to be done in this area.

In a variation of the cross-sectioning method a chip from a CdS cell was peeled from its substrate, fractured through its thickness direction, and the CdS at the exposed edge was etched away as before. The sample was examined in the SEM, with varying degrees of tilt, but the results were not encouraging. Since the fracture of these structures is conchoidal, and the depth of the focus of the SEM is large, it is very difficult to distinguish between the Cu₂S at the exposed edge and the CdS below the edge.

3.1.3 Replication

An alternate method (and an advantageous one) of examining the Cu₂S layer structure is replication. This method surmounts the difficulties of breakage in handling the free-standing Cu₂S layers, and allows for the practicality of cross-sectioning the replicas for quantitative characterization of the geometry. Replication was accomplished by leaching away the Cu₂S layer from a Cu₂S/CdS thin film solar cell in KCN solution (65 gms/liter), applying a commercial plastic replicating material to the exposed surface, and then etching away the CdS in dilute HCl as before. After coating the plastic replica with Au or C for charge dissipation, the structure was examined in the SEM. Some replicas tended to soften and distort from the heat of the examining electron beam, while others were reasonably resistant to heating effects.

Figure 1 shows two magnifications of a replica of the Cu₂S/CdS interface of a low output (3.4% efficient) Cu₂S/CdS cell. The technique has been successful in replicating the detailed configuration of the Cu₂S/CdS interface, comparable to what was observed for free-standing Cu₂S layers as reported in the previous quarterly progress report. While the spatial resolution is excellent, it is not clear that the curvature

of some of the peaks seen in Figure 1 is a true representation of the actual Cu_2S structure of whether distortion has occurred after separation from the CdS. Some curvature of the columnar peaks has been observed on free-standing Cu_2S films. Replication of the $\text{Cu}_2\text{S}/\text{CdS}$ interface could be a convenient and effective means for examining the structure of Cu_2S layers of cells, but further work is needed to ascertain the success of this technique.

3.1.4 Structural Differences of Cu_2S Layers

As noted in the previous report, higher output cells made in this laboratory have generally been characterized by a high density of deep etch pits and a high degree of pyramiding of the tops of the CdS crystallites at the front surface (both of which result from the HCl etch prior to barrier formation), and also by deep penetration of the Cu_2S into the CdS film. The taller features of Figure 1 correspond to regions in which the Cu_2S formed on the walls of deep etch pits, while the shallower honeycomb-like features between peaks are sheet-like penetrations of Cu_2S into the boundaries between grains from the front surface.

3.1.4.1 Penetration into Etch Pits

In Figure 2 SEM pictures are shown of the underside of the free-standing Cu_2S layer of a higher output cell (5.2% conversion efficiency, 19.0 mA/cm^2 short circuit current density). Comparing Figures 1 and 2 and discounting the broken tops of the peaks of Figure 2 (which are artifacts of sample preparation) one can see that there are about the same number of "peaks" per unit area, all of which appear to be about the same height. However, the peaks of the specimen from the lower output cell taper more and have less side branching (i.e., lateral penetration of the Cu_2S from the walls of the etch pits into intersecting grain boundaries). The cell of Figure 1 has lower current ($11.8 \text{ vs. } 19.0 \text{ mA/cm}^2$) than that of Figure 2. The structural details of the Cu_2S -CdS interface in the low output cell of Figure 1 were attributed to inadequate

(a)

(b)

Figure 1. Fax film replica of $\text{Cu}_2\text{S}/\text{CdS}$ interface of low output cell
viewed from underside - Cell #585-5 ($\eta = 3.4\%$, $J_{\text{SC}} = 11.8 \text{ mA/cm}^2$)

(a)

(b)

Figure 2. Free standing Cu_2S layer of high output cell viewed from underside - Cell #562-8 ($\eta = 5.2\%$, $J_{\text{SC}} = 19.0 \text{ mA/cm}^2$).

agitation of the CuCl solution during barrier formation. This would cause depletion of Cu^+ ions in the solution locally in the etch pits during the short dip time, and result in less penetration of the Cu_2S into the intersecting grain boundaries from the sides of the etch pits.

While the lower output of some cells may be attributed to deficiencies of the barrier dipping process, as in the case in the example discussed above, others cannot be. It has been found that high current densities cannot be obtained from some CdS films even though a wide range of etching and dipping conditions are tried. In these cases there must be some characteristic inherent in the CdS film itself which prevents realization of high cell output. Moreover, it now appears, in the above examples, that differences in the way these films form deep pits during pre-barrier etching may account for differences in cell output. For instance, CdS films fabricated in this laboratory on molybdenum foil substrates have invariably yielded cells with short circuit current densities below 15 mA/cm^2 . An examination of a number of such films disclosed that fewer deep etch pits were developed on those films during the pre-barrier etching step, and that the etch pits seemed to be shallower. Figure 3 is an SEM picture of a typical CdS film on molybdenum foil substrate after receiving the standard pre-barrier etch (7 seconds in 2:1 HCl at 45°C). By comparison, Figure 4 shows the etch pattern of a standard process CdS film on a zinc plated copper substrate after the same etching procedure. The film on a molybdenum substrate was more highly textured than that on a standard copper substrate, but it had significantly fewer etch pits per unit area.

Figure 5 shows the etch pit pattern of a CdS film that was deposited onto a zinc-plated copper foil substrate which had been chemically polished prior to zinc plating. The chemical polishing was an attempt to smooth the surface of the substrate in the hope that this would lead to better structured CdS films and thence to higher output cells. It can be seen that there are fewer etch pits per unit area on this film, as compared with the standard process film shown in Figure 4, and that they tend to be bunched rather than evenly dispersed. This

Figure 3. Typical CdS film on molybdenum substrate after standard HCl Etch. Gives low output cells ($J = 10$ to 15 mA/cm^2 ; $\eta = 2$ to 3%).

Figure 4. Typical CdS film on zinc plated copper substrate after standard HCl etch. Gives higher output cells ($J_{SC} \approx 15$ to 20 mA/cm^2 ; $\eta = 5$ to 6%).

Figure 5. CdS film on zinc plated chemically polished copper substrate, after standard HCl etch. Gives low output cells ($J_{SC} = 12$ to 14 mA/cm^2 ; $\eta = 3$ to 4%). (Compare with Figure 4.)

Figure 6. Penetration pattern of Cu_2S into top surface of a "good" CdS film with no HCl pre-etch. CdS film #582 (which gave > 5 Cells) dipped for 6 seconds into boiling concentrated CuCl solution, then the Cu_2S was removed by immersion in KCN solution.

film yielded cells with current densities of 12 to 14 mA/cm² and efficiencies of 3 to 4%. Observations of the etch pit patterns of a number of cells of varying output levels seems to corroborate the hypothesis that high current output cells result when there is a high density of small, but deep and evenly dispersed, etch pits on the CdS film after the HCl pre-etch operation.

3.1.4.2 Penetration from Top Surface into Grain Boundaries

Examination of free-standing Cu₂S layers (or replicas of such layers) is best done with the sample tilted at about 45° to the primary electron beam, thus giving a perspective view. Unfortunately, that part of the structure representing the deep penetration into etch pits masks the structure representing the shallower penetration into grain boundaries from the front surface. One way to get a better view of the shallower penetrations in the grain boundaries is to process a cell without pre-etching and then to examine the Cu₂S structure--a method that was followed and was described in the previous quarterly report. It was found that without a pre-etch the Cu₂S does penetrate into grain boundaries from the front surface to depths of about 3 to 5μ and would occasionally penetrate to depths of as much as 10μ in places where several grain boundaries may intersect.

Recently, Baron, et al.⁽²⁾ reported leaching the Cu₂S from Cu₂S/CdS film cells and examining the remaining CdS film surface in the SEM. Areas where Cu₂S had penetrated were clearly delineated by a pattern of crevasses. We have used this technique to obtain a measure of the Cu₂S penetration in from the front surface of variously processed film cells. Figure 6 shows the pattern of Cu₂S penetration from the front surface of a "good" CdS film (i.e., a film which under standard process conditions yielded cells with greater than 5% conversion efficiency) when no HCl pre-etch was used. Since preferential Cu₂S penetration down grain boundaries has been assumed consistently in past work on these types of cells, it is convenient to consider the pattern of Figure 6, for the most part, as functionally delineating individual grains in the CdS film.

Two details about the pattern of Figure 6 must be noted, however. First, the preparation conditions used in obtaining this CdS film are generally considered to yield grains of about 1 μm size. A large fraction of the area shown in Figure 6 is associated with "grains" of much larger size, up to about 5 μm . Second, some of the lines in Figure 6 do not form closed areas. These lines could be attributed to physical irregularities of the CdS surface, as grown.* The light and dark shading in Figure 6 suggests the undulating topography of these films. The hillocks are about 10 to 15 μm in diameter and bear a correspondence to the topography of the substrate (which is determined by the grain structure of the copper foil).

Widely different patterns of Cu_2S penetration into grain boundaries have been observed on different cells, and even on different areas of the same cell. Figure 7 shows views of two other areas of the same film as shown in Figure 6. The pattern of small, somewhat regularly oriented, rectangular features in Figure 7(a) might have resulted from a built-in stress in a local region of the CdS film, possibly due to the topography of the underlying substrate. In Figure 7(b), it appears that one cluster of CdS crystallites has been affected by the CuCl solution appreciably more than the surrounding clusters.

When an HCl etch is used prior to Cu_2S formation, the pattern of the copper sulfide penetration does not appear to be significantly affected as shown in Figure 8(a). The surface topology is more complex, of course, due to the formation of etch pits and sub-micron texturing. A finer network of Cu_2S penetration (on a different CdS film than that used for the specimens of Figures 6, 7 and 8(a)) is shown in Figure 8(b) and (c). The latter gives a view showing that the Cu_2S penetration at crystallite boundaries is approximately normal to the film surface. The size differences in areas delineated by the Cu_2S etch-out method shown in Figures 6, 7 and 8 highlight the problems in assigning a functional size to the crystallites of CdS films. An accurate

*See for example the crevices of Figure 21 which are typical of an as-grown film.

(a)

(b)

Figure 7. Penetration patterns of Cu_2S into other areas on the same film as in Figure 6.

(a)

(b)

(c)

Figure 8. Patterns of penetration of Cu_2S into top surface of pre-etched CdS films (pre-etched for 7 seconds in 2:1 HCl @ 45°C , then dipped 6 seconds in concentrated CuCl solution at 100°C , then leached in KCN solution to remove Cu_2S). (a) Film 582 (used for specimen of Figure 6). (b) Film 586 at 0° tilt in SEM examination. (c) Film 586 at 45° Tilt.

modelling of behavior for a specific cell specimen in terms of crystallite size requires careful consideration of this matter.

3.2 Etching of CdS Films

Because of the importance of the HCl pre-barrier etch to cell output, some preliminary studies were carried out on the etching of CdS films in HCl. The immediate purpose was to determine how HCl attacks polycrystalline CdS films, particularly with regard to pyramiding (or "texturing") of the surface and with regard to deep etch pitting, and how these may vary with changes in etching parameters (concentration, time and temperature). While there are a number of studies reported in the literature on the etching of CdS (and other II-VI) single crystals, there is very little information on the etching of CdS polycrystalline films.

3.2.1 Effect of Time

Figure 9 presents views of the front surface of a typical CdS film (which yielded a 5.2%, 19.0 mA/cm² cell under standard process conditions) after 4, 5, 7, and 10 seconds of etch time in 2:1 HCl solution at 45°C. The major effect of increasing time, over this range, appears to be the degree of pyramiding of the individual crystallites. The number, lateral size, and spatial distribution of the etch pits do not appear to change appreciably with time. It is probable that the depth of the etch pits does increase with time since increasing etch time, as has been observed, tends to decrease the shunt resistance of cells processed from the etched films and increases incidence of short circuited cells.

3.2.2 Areas of Preferential Attack

The CdS films presently being made in this laboratory are deposited on the mat surface of zinc-plated electroformed copper foil substrates. Figure 10 shows an SEM picture of such a copper foil

(a) - 4 seconds etch time

(b) - 5 seconds etch time

Figure 9. Effect of Etching time in 2:1 HCl Solution at 45°C. Typical CdS film on Zn-Cu substrate.

(c) - 7 seconds etch time

(d) - 10 seconds etch time

Figure 9. Continued

Figure 10. Copper foil substrate (after light clean-up etch).

Figure 11. CdS film on copper foil substrate (after etching 2 minutes in 1:5 HCl @ 80°C).

substrate. The grain size is on the order of 10 microns. The CdS films deposited on these substrates are polycrystalline with preferentially oriented columnar crystallites on the order of 1 to 5 μm across. The "c" axes of the CdS crystallites are approximately perpendicular to the substrate (under normal growth conditions) while the three coplanar "a" axes are generally parallel to the plane of the substrate, with those of the various crystallites randomly oriented to each other. This structure has been described by Shiozawa, et al.⁽³⁾ and by others, particularly Boer et al.⁽⁴⁾ As was shown by Boer et al., the topography of the upper surface of the CdS film is a replica of the surface of the underlying substrate. Figure 11 shows an SEM view of a typical CdS film surface after light etching to develop pyramidal tops on the individual crystallites. It can be seen that the individual crystallites are arranged in clusters, also about 10 μm across (compare with Figure 10).

The 2:1 HCl solution used in the standard pre-barrier etching step attacks the CdS film so rapidly that areas of initial (or preferential) attack cannot be identified. A more dilute solution of 1:5 HCl was therefore used at room temperature in an effort to get a clearer picture of the way HCl attacks CdS films. Figure 12(a), (b), and (c) show three magnifications of the surface of a typical standard process CdS film on a zinc plated copper foil substrate after the CdS had been etched for 5 minutes in 1:5 HCl at room temperature. Randomly spaced clusters of grains appear which have been attacked preferentially. These are the lighter features in Figure 12(a), (b), and (c). When the specimen is examined at an angle (Figure 12(d)), it is seen that the light features are clusters which project more from the surface of the film than their neighbors, and that they are being attacked preferentially around the outer edges. It is to be noted in Figure 12(c) that each cluster of crystallites tends to be divided into several segments of canyon-like surface features and that these are similar in appearance to the pattern of the Cu_2S penetrations seen in Figure 6.

As the etching time in the 1:5 HCl increases, the clusters that had been preferentially attacked initially continue to be attacked.

(a)

(b)

Figure 12. The surface of a typical CdS film after etching for 5 minutes in 1:5 HCl solution at room temperature. Progressively higher magnification was used for the views shown in (a) to (d). For (d) the angle of electron beam incidence was changed as well.

(c)

(d)

Figure 12. Continued

Examples (not the same cluster) are shown in Figure 13 for which the etch time was increased to 10 and then to 20 minutes. It is to be noted also that the boundaries between crystallite clusters become more prominent with increased etching time.

As the etch time is increased further, the effects of preferential attack of random clusters of crystallites are lost. No trace of these clusters can be found. It had been thought earlier that the preferential attack would continue and that the end result would be a number of deep pinholes in the CdS film, probably reaching to the substrate. Such large pinholes were looked for on films etched for 40, 80 and 160 minutes, but could not be found. It now seems that these preferentially attacked "clusters" are the so-called growth anomalies observed in the low power optical microscope on all of the deposited CdS films. Etching merely levels these rather than undercutting them to leave pinholes as had been thought might be the case. It appears from these observations that the "growth anomalies" can probably be disregarded as having no measurably deleterious effect on CdS film quality. Spattered particles of CdS, which have a similar initial appearance, do cause pinholes and cannot be disregarded.

As the etching time is increased further, to 40, 80 and 160 minutes, small etch pits appear and get larger and more numerous. A few starting etch pits can just barely be discerned in the photos of Figure 13 after 10 and 20 minutes of light etching. They tend to be located at the boundary regions between crystallite clusters more than at the boundary regions between crystallites within clusters--but not entirely so. This can be seen more clearly in Figure 14. At this stage (160 minutes in 1:5 HCl at R.T.) many of the etch pits have enlarged enough to join others and thus form an elongated etch feature or crevasse. With this amount of light etching, the distribution and pattern of the etch pits appears to be roughly comparable to the distribution and pattern of the deep penetrations of Cu_2S as observed on free-standing Cu_2S layers from standard process cells. (Compare the etch pit pattern of Figure 14(b) with the pattern of deep penetrations of Cu_2S into a CdS film as seen in the free-standing Cu_2S layer of Figure 15.)

(a) - After 10 minutes of etching in 1:5 HCl at R. T.

(b) - After 20 minutes of etching in 1:5 HCl at R. T.

Figure 13. Crystallite clusters being attacked preferentially.

(a)

(b)

Figure 14. Etch pitting of typical CdS film after etching for 160 minutes in 1:5 HCl at R.T.

Figure 15. Free-standing Cu_2S layer of high output cell. Note that the pattern of deep penetrations corresponds roughly to the developing etch pit pattern of Figure 14(b) and to the grain pattern of the copper substrate of Figure 10.

Figure 16. Surface of typical CdS film after etching for 4 minutes in 1:5 HCl at 80°C . Compare with Figure 9(d).

The degree of etching reached at 160 minutes in 1:5 HCl at room temperature is still considerably less than what is achieved after 7 seconds in 2:1 HCl at 45°C. This is evident from the size of the etch pits and the degree of pyramiding (refer to Figure 9(c) for comparison). However, it is the developing pattern of the etch pits that is important. This pattern appears to correspond with that of clusters of crystallites and the grains of the underlying substrate.

The boundaries between crystallite clusters are attacked by the HCl solution more than the boundaries between crystallites within the clusters. This is probably because there is a high density of imperfections in these regions. The effect appears to be greater where three (or more) clusters intersect to form a more or less vertical pattern as shown in the SEM pictures of Figure 14.

3.2.3 Effect of Concentration and Temperature

The use of more dilute (1:5) HCl solution at room temperature, in place of the strong 2:1 HCl solution at 25°C, makes it possible to slow down the attack of CdS films so that the initial phases of the etchant attack of CdS films can be observed. This also permits observation of the attack as it occurs over a period of time. Qualitatively, it appears that the major effect of decreasing acid concentration and solution temperature is to slow down the action. Though the nature of the pyramiding of the tops of the crystallites, and the nature of the resulting etch pits appeared to be the same, the dilute HCl etching of CdS films could not be carried to the same end point because well before that end point was reached, the etchant penetrated to the underlying zinc layer on the substrate at some place on the film area. Because of the much greater reactivity of zinc in HCl it would undercut the CdS film and strip it from the substrate. Thus we were not able to etch any CdS films in 1:5 HCl at room temperature beyond 200 minutes.

However, it is possible to go beyond the degree of etching experienced in 1:5 HCl at room temperature for 160 minutes, by increasing

the temperature. For example, Figure 16 shows the surface of a CdS film etched for 4 minutes in 1:5 HCl solution at 80°C. This degree of etching seems to be comparable to what was experienced after 10 seconds of etching in 2:1 HCl solution at 45°C (compare Figure 16 with Figure 9(d)).

Other films have been etched in concentrated HCl (i.e., undiluted, or approximately 37% HCl) both at room temperature and at boiling temperature (approximately 57°C). Roughly, about the same degree of etch pitting was observed after 1 second of etching in boiling (57°C) HCl as was observed after 10 seconds of etching in 2:1 HCl at 45°C, as is evident in Figure 17. The pyramids and the etch pits seem to be better defined, and the etch pits appear slightly smaller and more numerous, but the overall effect is roughly comparable. Similar results were also obtained when a CdS film was etched for 4 seconds in concentrated HCl at room temperature, as can be seen in Figure 18.

One cell was fabricated from a CdS film etched for 1 second in boiling concentrated HCl, and one cell was fabricated from a CdS film etched for 4 seconds in concentrated HCl at room temperature. Both cells were 5.1% efficient, comparable to standard process cells made at the same time. However, it was difficult to repeat the results because of difficulties with short circuits. While cells could not be successfully fabricated from films with greater etch times in concentrated HCl, the films could be successfully etched and examined. This is useful in order to see how the etching process proceeds with time. Figure 19 shows a CdS film after etching for 16 seconds in concentrated HCl at room temperature. At this stage the etch pits comprise about half of the area of the film surface. About the same degree of attack was observed after 2 seconds in boiling concentrated HCl. It is noteworthy that the attack of scattered clusters of CdS crystallites, experienced at 5 to 20 minutes of etching in 1:5 HCl at room temperature, was also observed at 1 second of etching in concentrated HCl at room temperature, as can be seen in Figure 20 (compare with Figure 12(b)). However, at 2 seconds of etching (and longer) no such effects could be detected.

(a)

(b)

Figure 17. Surface of Typical CdS film after etching for 1 second in boiling concentrated HCl.

Figure 18. Surface of typical CdS film after etching for 4 seconds in concentrated HCl at room temperature.

Figure 19. Surface of typical CdS film after etching 16 seconds in concentrated HCl at room temperature.

(a)

(b)

Figure 20. Surface of typical CdS film after etching for 1 second in concentrated HCl at room temperature.

3.2.4 Electrolytic Etching

From the above experiences it appears that higher reaction rates, which are obtained by higher acid concentrations and higher temperatures, result in opening a greater number of widely dispersed etch pits. This is thought to be a favorable condition for obtaining an optically dense Cu_2S structure without having the Cu_2S film thickness much greater than the diffusion distance for minority carriers in the Cu_2S . However, the very fast reaction rates obtained by etching in hot concentrated HCl cause such a rapid attack of the CdS that control is very difficult and hence the yield of usable cells is very low. It was hypothesized that the rate of reaction could be increased by applying a potential to the CdS film during etching, and that control could be exercised by using dilute acid solutions at lower temperatures.

A number of experiments were carried out with etching of CdS films in 1:5 HCl solution at room temperature with various electric potentials applied to the CdS film. Potentials from -300 mV to +300 mV, as compared to a calomel reference electrode, were tried with the times varying from 5 seconds up to 20 minutes. Some scattered small etch pits were observed, and attacks of occasional scattered clusters of crystallites were also observed, but the results did not look promising for cell fabrication purposes.

However, when the potential was increased to +20 volts, a distributed pattern of small etch pits was observed after 5 seconds of etching. Figure 21 shows the start of the etch pitting process. These small etch pits tended to occur randomly across the surface of the CdS film instead of being concentrated at the boundaries between crystallite clusters. This can be seen in Figure 21. If these etch pits were developed further (as they possibly would, given more time or higher HCl concentration or higher temperature or a combination of these) it might well lead to a more efficient photon absorbing Cu_2S structure that could be obtained under more readily controlled operating conditions. This method conceivably could free this process from the present criticality of the substrate topography.

Figure 21. Surface of typical CdS film after electrolytically etching for 5 seconds in 1:5 HCl solution at room temperature with +20 volts of applied potential.

3.3 CdS Films Produced at Elevated Substrate Temperatures

In an effort to obtain films with substantially larger crystallites, films were grown at elevated substrate temperatures. The inner chamber hot wall deposition technique described earlier⁽⁵⁾ was used with molybdenum foil substrates. Zinc plated copper foil substrates cannot normally be used at temperatures above about 250°C because of the high vapor pressure of zinc. With molybdenum substrates, no zinc is required (to establish an ohmic contact and act as a diffusion barrier layer), hence very high substrate temperatures are possible. During this period, CdS depositions were carried out on molybdenum substrates at temperatures up to 450°C. (Depositions at temperatures up to 600°C have been reported earlier.⁽⁶⁾)

Some difficulties were encountered with control of the substrate temperature. The inner chamber walls had to be held about 100 to 150°C higher in temperature than the substrate, otherwise more of the available CdS deposited onto the chamber walls. However, radiation from the chamber walls caused the substrate temperature to climb above the control point. Usually the substrate temperature increased gradually during the deposition period after an initial jump in temperature at the onset of evaporation (from the source radiation).

A total of 19 hot wall deposition runs were carried out but most of these were for purposes of developing and for testing the tooling, and for calibrating the operating parameters. Four depositions were carried out at the end of the period which could be examined for grain size and measured for electrical resistance.

The results from these runs are summarized in Table I. Runs C-15 and C-16 used CdS charge material which had been pre-doped with 20 ppm of indium during sintering. The deposition of C-15 was carried out over a 25 minute period with the substrate temperature ranging from 360°C to 375°C and the chamber wall holding at 540 to 545°C. The CdS film was 20 μ thick. The deposition of C-16 was carried out over a 20 minute

period with the substrate temperature ranging from 350°C to 450°C and the chamber wall from 480°C to 550°C. This CdS film was 40 μ m thick. It is not understood why the latter film should have been twice as thick when the times and temperature should have made it thinner. The slightly higher source evolution rate does not seem to be enough to account for it. It seems possible in retrospect that an erroneous temperature indication might have occurred.

Table I

Parametric Data - Hot Wall CdS Film Depositions

Run No.	Ave. Substrate Temp	Ave. Wall Temp	Ave. Deposition Rate	Ave. Source Evolution Rate	Ave. Film Thickness	Ave. Film Resistance	Ave. Grain Size
C-15	368°C	543°C	133 $\overset{\circ}{\text{A}}$ /sec	5.3 mg/sec	19.8 μ	17,800 Ω cm	8.5 μ
C-16	418°C	535°C	333 $\overset{\circ}{\text{A}}$ /sec	7.5 mg/sec	39.9 μ	25,300 Ω cm	12.5 μ
C-17	423°C	580°C	150 $\overset{\circ}{\text{A}}$ /sec	7.1 mg/sec	17.5 μ	171,000 Ω cm	3.2 μ
C-18	391°C	545°C	100 $\overset{\circ}{\text{A}}$ /sec	2.6 mg/sec	11.7 μ	99,000 Ω cm	3.2 μ

Both films had substantially enhanced grain size. Figure 22 shows SEM views of these films after lightly etching in dilute HCl. The grain size of film C-15 varied from about 4 μ to about 15 μ and averaged about 8 μ . The grain size of film C-16 was appreciably larger varying from about 7 μ to about 18 μ and averaging about 12 μ .

By analysis, CdS film C-16 had 13 ppm of indium actually included in the grown film, but at 25,000 ohm-cm the resistance was much too high for cell fabrication. Therefore, the next two runs were made using CdS charge material that had 48 ppm of indium incorporated during the material sintering step. However, the resulting CdS films were even higher in electrical resistance. By analysis C-17 had only 10 ppm and C-18 had 20 ppm of indium in the deposited films. It appears that doping of these higher temperature CdS films must be greatly complicated by impurity segregation effects.

(a) - CdS film C-15, grown at 350/375°C.

(b) - CdS film C-16, grown at 350/450°C.

Figure 22. CdS films on molybdenum substrates (after etching 20 minutes in 1:5 HCl at R.T.)

Deposition run C-17 was carried out with the substrate varying from 400°C to 440°C and the chamber wall varying from 553°C to 595°C. Run C-18 was slightly cooler with the substrate at 360°C to 410°C and the walls at 535°C to 550°C. The resulting films, after 20 minutes of deposition were 18 μm and 12 μm thick respectively.

The grain size of the latter two films were delineated by dipping the films in hot CuCl solution to form Cu_2S and then removing the Cu_2S in KCN solution, as before. The grains were effectively delineated in this manner, as can be seen in Figure 23. However, unexpectedly, the grain size of films C-17 and C-18 were appreciably smaller than for the previous two films. The grains of both films ranged in apparent size from about 1 μm to about 6 μm and averaged about 3 μm .

From the above discussion, it appears that some parameter other than substrate temperature has a major influence on grain size. The same lot of molybdenum foil was used for all four depositions, and its preparation was the same in each case. It is evident that more extensive effort will be required to develop the process for making larger grained CdS films suitable for fabrication into cells.

3.4 Characterization of Minority Carrier Transport in Cu_2S Layers

3.4.1 Background and Theory

Work has continued on the measurement of the transport properties of the Cu_2S . The measurements are presently being done with single crystal CdS as the substrate, although preliminary work using polycrystalline CdS thin films as the substrate is encouraging.

As discussed previously,⁽¹⁾ for this technique the Cu_2S is formed by evaporation of CuCl onto the CdS through an aperture mask located at a fixed small distance above the substrate. This is followed by heating to convert the CuCl to Cu_2S . The result is a graded thickness layer of Cu_2S , similar to a beveled junction but with an extremely shallow bevel. An analysis of this region is accomplished by scanning with a He-Ne laser spot and monitoring the induced photocurrent.

(a) - CdS film C-17, grown at 400/440°C.

(b) - CdS film C-18, grown at 360/410°C.

Figure 23. CdS films on molybdenum substrates (after dipping 6 seconds in concentrated CuCl solution at 100°C and then removing Cu_2S layer in KCN solution - no pre-etch).

Initially, the sample was analyzed by repeated scanning while monitoring the photocurrent, the reflection and the transmission (as measured by a detector behind the sample). The transmission data was converted into a thickness profile of the Cu_2S by correcting for reflection losses and by assuming an absorption coefficient value. The data was fitted to a theoretical curve of photocurrent versus thickness of the Cu_2S . This involved considerable analysis for each sample. An improved procedure has been implemented which involves displaying the photocurrent versus transmission information directly on a CRT. The data can be obtained in this form by using the output of the photodetector mounted behind the sample, to drive the horizontal sweep of the oscilloscope. A typical example of such a curve is shown in Figure 24.

Theoretical curves of response as a function of thickness are obtained by solving, with appropriate boundary conditions, the equation for electron concentration in the Cu_2S -p type layer for monochromatic excitation:

$$D_n \frac{d^2(\Delta n)}{dx^2} - \frac{\Delta n}{\tau} = -\alpha I_0 \exp(-\alpha x) \quad (1)$$

where D_n = diffusion constant for electrons
 α = absorption coefficient
 τ = electron lifetime
 Δn = excess electron concentration
 I_0 = flux of photons into the Cu_2S

Several workers have given solutions to Equation 1 for special cases. (3), (4) Results are usually presented in the form of logarithm of photocurrent as a function of Cu_2S layer thickness (see Figure 18 in Reference 1). Values of film thickness can be converted to transmission (T) through the Cu_2S layer by the expression:

$$T = \exp(-\alpha t) \quad (2)$$

Theoretical curves for selected values of diffusion length and surface recombination velocity (SRV) are shown in Figure 25. For infinite

Figure 24. Oscilloscope trace of photocurrent versus transmission for a tapered Cu_2S film on single crystal CdS . Vertical and horizontal scale: 10^{-6} a/maj. div. ($100\% T = 8 \times 10^{-6}$ a). Origin is at light spot, lower left corner.

length (no electronic losses) and $SRV = 0$, a straight line is predicted:

$$I_{\text{photo}}/I_{\text{photo,max}} = A = 1-T \quad (3)$$

where A is the absorption occurring within the Cu_2S . Considering the location of the peak response for various diffusion length values for the case of no surface recombination (right hand panel of Figure 25), one can observe that as the diffusion length is decreased from $0.6 \mu\text{m}$ to $0.2 \mu\text{m}$, the peak response occurs at progressively larger transmission values in the 15 to 34% range. This corresponds to a change in thickness of the Cu_2S for optimum collection from $0.38 \mu\text{m}$ to $0.22 \mu\text{m}$. At sufficiently high values of transmission (film thickness $\lesssim 0.07 \mu\text{m}$) the predicted rate of change of photocurrent with transmission is not sensitive to the value of minority carrier diffusion length. For fixed minority carrier lifetime (e.g., $L = 0.4 \mu\text{m}$) the effects of increasing values of surface recombination velocity (left panel of Figure 25) are (1) suppression of peak amplitude of current response, (2) a change in the rate of photocurrent decrease with transmission for $T \gtrsim 70\%$ and a slight shift of the transmission value for peak response (e.g., from 21 to 25% for the example in the left panel of Figure 25).

The primary advantage of this approach to the Cu_2S response is in the case of obtaining and treating the data. The shape of the current response-transmission curve is independent of the shape of the evaporated "wedge" structure. Local non-uniformity in the thickness of the wedge structure is common. This method, since it is insensitive to this variation, can provide a more direct measure of changes in the Cu_2S response. By moving the scanned region across the sample, it was determined that the uniformity, as measured by the peak of the response, is quite good across a single sample.

3.4.2 Experimental Results

The solid curve in Figure 26 gives results for a scan of one specimen using a single crystal substrate polished on both sides.

Fig. 25 — Theoretical response of $\text{Cu}_2\text{S}/\text{CdS}$ cells as a function of transmission of light at $6328 \text{ \AA}$

CuCl was evaporated⁽⁵⁾ through a raised aperture mask to yield a "wedge" structure (tapered thickness layer). This was converted to Cu₂S by heating at 180°C for 10 minutes in flowing N₂. The sample was rinsed in methanol and blown dry. The laser scanning equipment described previously⁽⁵⁾ was used. Calibration of beam power was made against a silicon standard cell and corrections for reflection losses were made.

The peak response of 46% occurred at a transmission value of 39%. A theoretical curve for $L_n = 0.2 \mu\text{m}$ and $\text{SRV} = 0$ is also shown. A value of $L_n = 0.4 \mu\text{m}$ and $\text{SRV} = 10^4 \text{ cm sec}^{-1}$ would have the same maximum response of 46% but the peak response would occur for 26% transmission.

The experimental curve is more steeply peaked and drops more sharply in the thicker Cu₂S region (low T) than the theoretical ones. The structure in the curve and deviation from the theoretical curve at high values of T might be due to reflection from the back surface.

3.4.3 Effects of Heat Aging

The effects of a 250°C two minute heat treatment in air are quite drastic. Figure 27 shows the photocurrent transmission behavior for the same sample as Figure 26 but after the heat treatment. With no bias light, the peak photocurrent response is down by approximately a factor of 200. However, the peak of the curve has shifted only slightly, occurring at 46% transmission as opposed to 39% for the unheated sample. The structure in the curve is much more pronounced and a second peak appears for $T \approx 74\%$. The height of the primary peak is 0.26% versus 46% before heating. The shift of the peak could be explained by a small decrease in the minority diffusion length after heating from $0.2 \mu\text{m}$ to about $0.18 \mu\text{m}$. Normally such a change would involve a drop in the peak normalized photocurrent only to 30% from 46%. The factor of ~ 200 reduction is attributed to reduced heterojunction collection efficiency produced as a result of the heating.

The effect of adding a white bias light is shown in the bottom curve of Figure 26. There is a strong enhancement in the photocurrent

Curve 713181-A

Fig. 26 — Experimental results for $\text{Cu}_2\text{S}/\text{CdS}$ cell with tapered Cu_2S thickness

Figure 27 — After heating for 2 min. at 250°C in air no bias light

response and the curve appears to peak at about 68% T. The curve at high T is parallel to that for the unheated curve but displaced downward, indicating degradation of heretofore collection efficiency of about 25% when compared to the peak before heating.

It is assumed that the bias light influence is due to its spectral content at shorter wavelengths ($\sim 5000\text{\AA}$). This light has a much higher absorption coefficient. The peak in the bottom curve of Figure 26 is attributed to the failure of the bias light's penetration to the junction and its inability to allow enhanced collection as the laser spot is scanned to thicker Cu_2S regions. The lack of activation at these thicker regions rapidly drops the photocurrent response.

The fact that the slope of the curve after heating is comparable to the original curve implies that the losses are not connected with those involved in Cu_2S transport but rather are in the junction region.⁽⁵⁾ Assuming a total collection efficiency given as

$$\eta = \eta(\text{Cu}_2\text{S}) \cdot \eta(\text{J}) \quad (4)$$

where $\eta(\text{Cu}_2\text{S})$ is the collection associated with Cu_2S , and $\eta(\text{J})$ is the collection at junction (light sensitive).

On the unheated sample, $\eta(\text{I}) \approx 1$ since $\eta \approx \eta(\text{Cu}_2\text{S})$. For the post-anneal sample, assuming that $\eta(\text{Cu}_2\text{S})$ remains unchanged $\eta(\text{I}) \approx .05$ for low bias light intensities. If the peak for the post-heating light bias curve is due to the thicker Cu_2S and assuming that no change occurs in $\eta(\text{Cu}_2\text{S})$ between the light bias and no light bias case, then it can be concluded that the decrease in the curve at the higher values of T occurs because of a change in $\eta(\text{I})$ from 1.0 to 0.78.

The primary effect of heating has been a decrease in the junction collection efficiency of approximately 20%. The unheated sample had $L_n \approx .2$ with $\text{SRV} \approx 0$ while after heating, L_n decreased only slightly.

The errors associated with this technique appear to be primarily in the calibration of 100% transmission and corrections for reflection

losses. The samples were carefully prepared to minimize non-uniformities in the CuCl layer and to allow direct measurement of the transmission for the base portion of the CdS crystal. Any errors of the type mentioned affect the absolute magnitude of L_n . Changes in the electronic properties of the same sample should be easily detected as long as there are no gross changes in optical properties as a result of heating. There is no evidence that these changes occurred in the sample studied.

3.4.4 Application to Polycrystalline Films

This technique does appear to yield useful information about carrier transport in the Cu₂S and collection by the junction. To apply this information, it will be necessary to use it on the thin polycrystalline film with the limitation that the cell would still be formed by the dry CuCl process.

Two problems appear in using thin CdS films. The surface of the film is textured which will present problems for correction of the losses associated with reflection. Also, the present method of measurement of the Cu₂S thickness relies on measuring light transmission through the film. The thin films are deposited onto an opaque substrate and are highly stressed, making removal difficult.

Some experiments have been initiated to evaluate the extent of these problems. The initial experiment consisted of measurements made on small area CdS cells, which had been cemented to a rigid backing plate. A CuCl of tapered thickness was evaporated and converted to Cu₂S as in the single crystal CdS case. A laser scanned photocurrent response curve as a function of position (along the taper) is shown in Figure 28. The results are quite good. There is not much more noise involved than in the signal from the single crystal CdS cell. Irregularities due to the unetched polycrystalline film appear small enough to be averaged over the beam spread. (One major division is approximately .007" in the figure.) The maximum CuCl thickness, as evaporated, corresponded to approximately 5000^oÅ equivalent Cu₂S thickness, as determined from optical measurements on a single crystal CdS.

Figure 28. Oscilloscope trace of photocurrent (arbitrary units) versus position for a $\text{Cu}_2\text{S}/\text{CdS}$ structure using a polycrystalline CdS film. Horizontal scale: $150\text{ }\mu\text{m}/\text{div}$.

To estimate a diffusion length value, it is necessary to know the exact thickness of Cu_2S at the peak of the response. There are two possible methods for obtaining this thickness. One is to use a control CdS single crystal sample which can be used as a calibration sample while the second is to perform optical transmission measurements after separating the film from the substrate or opening a small hole in the substrate. Since the film is highly stressed, these approaches are difficult and require the use of very small samples. However some preliminary experiments indicate that, with care, the film can be separated from the substrate and kept intact for direct measurements of optical transmission.

3.5 Light Bias Measurements

In attempting to measure the effects of heat treatment on the electronic properties of the Cu_2S , it was obvious that the change in light activated junction collection efficiency is one of the dominant mechanisms in the degradation of cell performance with time and heating. In order to obtain some measure of this spectral dependence of the light enhancement effect, a phase sensitive detection system was set up, as shown in Figure 29. This differs from more conventional systems by limiting the chopped light to the spectral range which should not affect the cell. In this case, it was filtered by a Wratter 88 filter which passes light above about $7800\text{\AA}$. The bias light passes through a monochromator before hitting the cell.

In operation, the chopped signal, detected with a lock-in amplifier, is a few percent of the intensity of the unchopped bias light signal. The chopped signal is a measure of the enhancement value of the bias light and since the chopped light is only a small portion of the bias light, the bias light becomes a measure of total cell response. The chopped light can be used to normalize the bias light response and correct the response for junction effects. The resulting signal gives a collection associated with the active region. Assuming that the collection is limited to the Cu_2S , we could use it to calculate the transport in the Cu_2S . However, this requires a planar structure and a well established absorption

Figure 29 — Block diagram for measuring effects of bias light

versus λ curve. Though this system is now being evaluated, the system is presently considered most useful to monitor the changes in junction heating.

Figure 30 is a curve of a heat-treated single crystal CdS substrate with a dry process CuCl layer equivalent to approximately 2000Å Cu₂S. The sample had undergone the standard dry process formation (180°C for 10 minutes, wash in methanol and dry). This sample also had a 250°C, 2 minute anneal in air. There is a very intense, very narrow response at 510 nm. This data was taken point by point to allow the signal to reach steady state. There is a very long time constant associated with the signal. The lack of any "quenching" at above 600 nm is reasonable since this is usually explained by assuming that traps are being emptied. Allowing sufficient time for each measurement allows the traps to be emptied thermally, which, in turn, results in the absence of a quenching signal.

Further work is planned using this technique to analyze the changes in the cells associated with degradation. Preliminary indications are that this enhancement effect is not necessary for attaining full open circuit voltages. Cells have been made with V_{OC} values of 0.48V (AMI) which exhibit no enhancement effect. These same cells, when heated further, exhibit an increasing light enhancement although there is no change in the open circuit voltage.

3.6 Delineation of Small Area Test Cells

3.6.1 Apiezon Masking and Mesa Formation

In the previous work on this program, most measurements of cell performance had been made using thin film devices of 2 cm x 2 cm size. Occasionally cells of 1 cm² area were used. With such large devices it becomes difficult to assess the role played by structural features, such as grains and etch pits. This is particularly important when the size distribution and density of the features are not under complete, direct control as regards film preparation and cell processing. As a result, it

Curve 713750-A

Figure 30 — Enhancement effect of bias light on a heat aged (2 mm, 250°C in air) self-structure produced by dry processing for Cu_2S formation on single crystal Cd S

has been difficult to obtain significant and reproducible correlations between preparation and processing parameters on one hand and cell performance on the other. It is clear that local evaluation of electrical behavior and cell performance is desirable.

The first approach at local measurement on a cell structure involved making probe contact to the Cu_2S layer with a pointed tungsten wire attached to a micromanipulator stage. In this case the high sheet resistance of the Cu_2S layer provided a degree of localization of area of response in the cell. On a film sample of 2 cm x 4 cm size, four distinct regions were delineated. Within each region, uniform probed behavior of one of the following types was observed:

- Type A: low, reverse saturation current under dark conditions, high photocurrent ($I_{\text{SC}} \sim 1$ to 2.5 mA) for AM1 illumination.
- Type B: lack of saturation of reverse dark current low photocurrent ($I_{\text{SC}} \sim 0.5$ to 0.7 mA) for AM1 illumination.

In addition, near the boundaries between Type A and Type B behavior, open circuit voltage values were generally lower by 10 to 90 mV for the Type A (higher photocurrent) characteristics. Since the series resistance presented by the Cu_2S layer was high, the illuminated behavior gave poor fill factor, with I_{SC} being only an indicator of total collected photocurrent. Nonetheless, from the approximate photocurrent inferred from the two types of behavior, it is estimated that current collection occurred from regions at least 0.2 to 0.6 cm in radius. The change in type of dark current behavior could be discerned over distances as small as 0.1 to 0.2 cm. These results made it clear that local variations in cell characteristics could be detected electrically by the probe methods. Furthermore, the variations involved parameters, viz. reverse impedance and short circuit current density, important in determining photovoltaic performance of large area cells.

Probe characterization is limited in its quantitative value for rationalizing the performing of a large area cell. As mentioned above, there is no simple method to determine the area which is responsive.

Illumination through an aperture mask is a possibility, but then the illuminated area acts as an electrically non-linear load shunting the active area. Extraction of photovoltaic parameters from such measurements, e.g., V_{OC} , J_{SC} , fill factor, becomes complicated. A more direct route is to physically isolate small regions of the large area cell and to characterize these independently.

A method of forming small area cells was applied to the specimen which gave the results described above. Dots of Apiezon wax were used to mask regions of various sizes. Most were about 0.05 cm across but the size range was 0.002 cm to 0.25 cm. The exposed Cu_2S layer was etched in 1M potassium cyanide. On removal of the Apiezon wax in trichloroethylene, small isolated cell regions were available for evaluation. Primarily the experimental results were: Low reverse saturation current under dark conditions was observed in both Type A and Type B regions, as designated on the basis of probed behavior before mesa production. Open circuit voltage values were approximately equal for mesas in either type region. This meant that the lower open circuit voltage values originally observed in Type A regions probably resulted from highly local regions which were removed by mesa formation. It was difficult to compare short circuit current densities for small cells in Type A and Type B regions since the mesas were irregular in shape and varied in size.

The use of wax masks and KCN etching was applied to another thin film Cu_2S/CdS specimen. In this case the mesa size was not varied deliberately. Thirty mesas (approximately $0.05\text{ cm} \pm 0.02\text{ cm}$ in diameter) were delineated in an array over the specimen area of $2\text{ cm} \times 4\text{ cm}$. When initially characterized, 83% of the mesas exhibited good saturation of dark current (similar to Type A probed behavior in the earlier specimen). A typical example is shown in Figure 31(a). The remaining mesas exhibited non-saturated reverse current (as in Figure 31(b)) or low fill factor. These results, representing a more complete scan of the specimen area those those described earlier, indicate the value of small mesa characterization to assess the uniformity of behavior for thin film Cu_2S/CdS cells.

(a) - Mesa #2A

(b) - Mesa #3A

Figure 31. AMI behavior of Cu_2S -etched mesa cells using a standard processed $\text{Cu}_2\text{S}/\text{CdS}$ film (#568-7/2). (a) Behavior typical of 83% of the mesas. (b) Poor behavior illustrating excessive shunt conduction.

It was a matter of curiosity to determine the influence of hydrogen annealing on the behavior of the mesa cells. After an 18 hour treatment in hydrogen at 180°C, the behaviors of Figure 32 were produced (corresponding to the two cells characterized in Figure 31). The most striking effect of the hydrogen heat treatment was to produce good saturation of the reverse current of the poorer cell (Figure 32b), resulting also in an improvement of fill factor. Open circuit voltage was improved as well. For the mesa with good initial saturation current, the open circuit voltage is improved somewhat but the fill factor is reduced (Figure 32a). Qualitatively, both devices are very similar after the hydrogen treatment. The fill factor after treatment may reflect a somewhat higher series resistance from the single probe contact to the Cu₂S layer.

Another result of the heat treatment was a strong "cross-over" effect, reflecting large suppression of dark forward current which is evident in Figure 32(a) and (b). This effect was not constant, since the dark forward current of a device biased at fixed voltage increased rapidly with time. When fit to an exponential time dependence, the change in forward behavior had a dominant time constant of about 10 minutes. It is interesting that the illuminated behavior exhibited no significant change correlating with the change in forward behavior.

The foregoing discussion has highlighted the value of small area cell structures in providing useful information on local behavior of thin film Cu₂S/CdS cells. The major disadvantages of the wax masking and Cu₂S etching technique lies in the tedium of masking large arrays of small mesas and in the difficulty of accurately controlling the size of mesas. The use of photolithographic methods common to silicon integrated circuit fabrication provides a means of mitigating these factors.

3.6.2 Photolithographic Processing

The use of photolithographic methods is attractive to delineate the active area of small Cu₂S/CdS thin film cells to be used in assessing

(a) - Mesa #2A

(b) - Mesa #3A

Figure 32. Influence of hydrogen annealing (18 hr, 180°C) on the behavior of the mesa cells of Figure 31 showing suppression of dark forward current and of the excessive shunt conduction in Mesa #3A.

material and structural uniformity over regions of interest for state-of-the-art cells. In addition, the availability of many small area cells on a substrate opens the possibility of selectively modifying the treatment of adjacent cells as a means of inferring sensitivity to process parameter variation. Before implementation of such an approach however, it was necessary to establish the chemical and physical effects (if any) on cell performance of the use of photoresist materials, including solvents, and of the heat cycles required for photoresist baking.

An experiment was conducted using Shipley AZ and Waycoat photoresist coatings to determine if these materials and their associated processing had any deleterious effect on thin film $\text{Cu}_2\text{S}/\text{CdS}$ cells. Three pieces of CdS film material on zinc plated copper foil were processed, two with the photoresist coatings and one as a control. (All three pieces were from the same deposition run, known to give cells of about 5% efficiency under standard processing.) Table 2 gives the sequence of steps to which each sample was subjected. In the case of photoresist processing, the window opening in the photoresist was somewhat larger than 1 cm x 1 cm. Cell performance was evaluated on each piece using a pressed contact grid over an area 1 cm x 1 cm in size. There were no significant differences in values of short circuit current density, open circuit voltage or fill factor between the control and the photoresist processed specimens. It can be concluded then that the chemical and temperature conditions to which the texture-etched CdS region is subjected in the use of Waycoat or AZ resists do not adversely affect the subsequent formation of the Cu_2S layer by the wet CuCl dip process.

To date several process variations have been used with the photoresist materials described above in making arrays of small cells. The simplest approach is to take CdS films without HCl texture etching and to apply Waycoat IC material in a so-called window frame pattern which defines exposed areas of CdS. The specimens are then given the standard CuCl dip, rinse and heat treatment to form Cu_2S layers, and hence active cells, in the open windows. Gold electrodes can be subsequently evaporated through an aperture mask to produce an array

Table 2. Processing Steps for Assessing Influence of Photoresist Use Prior to Cu_2S Layer Formation

Control	AZ-J Resist	Waycoat IC Resist
	<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="width: 30%;">←</div> <div style="width: 40%; text-align: center;"> <div style="border: 1px solid black; padding: 5px; margin: 0 auto; width: 80%;"> HCl Texture Etch 7 sec in HCl:H₂O::2:1 @ 45°C </div> </div> <div style="width: 30%; text-align: right;">→</div> </div>	
Store	<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="width: 30%;">←</div> <div style="width: 40%; text-align: center;"> Apply Resist </div> <div style="width: 30%; text-align: right;">→</div> </div>	
	<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="width: 30%;">←</div> <div style="width: 40%; text-align: center;"> <div style="border: 1px solid black; padding: 5px; margin: 0 auto; width: 80%;"> Pre-bake 90°C, 15 min </div> </div> <div style="width: 30%; text-align: right;">→</div> </div>	
	<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="width: 30%;">←</div> <div style="width: 40%; text-align: center;"> <div style="border: 1px solid black; padding: 5px; margin: 0 auto; width: 80%;"> Expose and develop resist for removal from ~ 1 cm x 1 cm area </div> </div> <div style="width: 30%; text-align: right;">→</div> </div>	
	Post Bake 120°C, 10 min	Post Bake 165°C, 15 min
	<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="width: 30%;">←</div> <div style="width: 40%; text-align: center;"> <div style="border: 1px solid black; padding: 5px; margin: 0 auto; width: 80%;"> Light HCl etch 1 sec in HCl:H₂O::1:2 @ 25°C </div> </div> <div style="width: 30%; text-align: right;">→</div> </div>	
	<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="width: 30%;">←</div> <div style="width: 40%; text-align: center;"> <div style="border: 1px solid black; padding: 5px; margin: 0 auto; width: 80%;"> Cu₂S Formation 6 sec in CuCl solution @ 100°C Water Rinse 250°C, 2 min Bake </div> </div> <div style="width: 30%; text-align: right;">→</div> </div>	
<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="width: 30%;">←</div> <div style="width: 40%; text-align: center;"> Test with Pressed Grid </div> <div style="width: 30%; text-align: right;">→</div> </div>		

of cells of varying sizes and grid geometries as shown in Figure 33. In a variation on this theme, instead of a standard dip in CuCl solution for the Cu₂S layer preparation, a much shorter immersion time has been used initially. Selected cells are covered with drops of AZJ resist which is fully developed and baked. The process is then repeated several times yielding an array of small cells whose CuCl immersion time varies. After stripping of the AZJ resist material in acetone (which does not affect the Waycoat IC film) heat treatment produces cells nearly identical in preparation except for the CuCl immersion time. Interesting results in terms of detailed photovoltaic response are presented for such a specimen in the next section.

Several factors have hampered the use of photoresist to form small cells with the essential features of the standard process. The application of Waycoat IC to previously textured CdS cannot mean simply a definition of small cell areas of the type shown in Figure 33. Protection of the highly textured surface by the resist film during CuCl immersion is poor. Cu₂S is formed in the window frame areas, thus preventing definition of small, isolated cells. It is also not possible to use this coating on unetched CdS during the high temperature HCl etching step. The CdS is severely attacked through pinholes in the resist causing mask failure during this step. A similar result was produced when a patterned film of evaporated silicon monoxide was used as the mask. Recently successful masking against the HCl texture etch was provided by such a patterned oxide layer with an overcoat of patterned Waycoat IC resist. In this case, the oxide is unaffected by HCl attack through pinholes in the photoresist. Of course the probability of coincident pinholes in the resist and oxide layers is very low, eliminating significant attack of the CdS in the masked region.

With the etch and chemical resist methods developed for small cell formation it should now be possible to design matrix experiments to evaluate cell processing influences. In the next section results of sequential matrix studies for various CuCl immersion times are discussed. In the future multi-dimensional matrices might be examined.

Figure 33. Example of cells produced on an unetched CdS film by photoresist (Waycoat IC) delineation of the areas for wet formation of the Cu_2S layer. Electrode patterns were applied by gold evaporation through an aperture mask.

One of immediate interest involves duration of the HCl texture etch step as one dimension and CuCl immersion time as another.

3.7 Process Influences on Behavior of Small Test Cells

3.7.1 Unetched CdS Films

Waycoat IC photoresist was applied to an unetched CdS film and processed to yield a window/frame mask as described in Section 3.6.2. Cells of nominal 0.1, 0.01, and 0.0006 cm² area were produced in the windows after immersion in CuCl at 90°C, rinsing in water and subsequent heating at 250°C for 2 minutes in air. To investigate the effect of CuCl immersion time, after the first 5 second immersion two modules containing a group of cells covering the entire size range were masked with a drop of Shipley AZJ resist, which was baked at 120°C for 10 minutes. After an additional 15 second immersion in CuCl for the remaining exposed cell areas, two more modules were masked off. This was repeated until four groups of cells had been prepared with net CuCl immersion times of 5 seconds, 20 seconds, 60 seconds and 140 seconds. After stripping of the AZJ resist layer in acetone (which left the Waycoat IC layer intact), the specimen was heated for 2 minutes at 250°C in air to form the Cu₂S layers in the variously treated cell areas. Although the intermediate heating during curing of the AZJ layers may have an effect, the major influence on cell behavior was expected to be the duration of CuCl immersion.

Figure 34 gives the detailed behavior of small area cells when subjected to quartz-halogen illumination ranging from ~ 50 to 1000 mW/cm². (Simulated AM1 conditions are indicated by the circled data points.) The two top curves are for the case of 5 second immersion, with the lower one being typical. The lower ideality factor for the low range of illumination, and the correspondingly higher values of V_{OC}, are taken to indicate that higher cell performance may be possible with short CuCl immersion times.

The four lower curves in Figure 34 suggest that immersion time has a regular, relatively simple influence on cell behavior.

Curve 713179-A

Fig. 34 — Photovoltaic behavior for a range of illumination of small, thin film cells produced by varying the immersion time in 90°C CuCl solution during Cu_2S layer preparation using a single, unetched CdS film specimen

Constancy of slope for less than 30 μ a of photocurrent indicates no significant change in cell current transport. The decrease in V_{OC} at constant photocurrent is taken to indicate the introduction of a larger diode opposing current with increased immersion time. This may simply reflect greater penetration of the final Cu_2S layer along grain boundaries, with a larger total area for the heterojunction. It is likely that the 60 and 140 second immersion times result in some local penetration of the Cu_2S along grain boundaries to the metal back contact. Many cells examined for these dip conditions exhibited high shunt conductance and could not be evaluated meaningfully. It was for this reason, also, that the smallest test cells ($\sim .10$ cm x $.006$ cm strips) were used for the characterizations of Figure 34.

After the initial characterization of the small strip cells used for Figure 34, we evaporated gold electrodes using an aperture mask. Significant broadening of the electrodes occurred because of the penumbra effect arising from lack of intimate contact between mask and substrate. As a result the electrically active areas of all the cells were smaller than the original design. In the case of the strip devices characterized in Figure 34, the electrode pattern was such as to connect eight adjacent strips as a single cell. For these cells the ratio of electrode shaded-to-active area was very large, causing about 10 mV reduction in V_{OC} from the pre-gridding behavior. Otherwise, for the cells immersed in $CuCl$ for 5 seconds and for 60 seconds, respectively, there was no significant change in behavior produced by gridding. For the cell dipped for 20 seconds, after gridding higher n-factor and lower V_{OC} values were noted for illumination of 200 mW/cm^2 or less. This suggests that one or more of the component strips for this cell was much poorer in performance than the unit characterized in Figure 34. The cell produced by 140 second immersion in $CuCl$ demonstrated poor behavior under AM1 conditions. This probably resulted from local penetration of Cu_2S down the grain boundaries to short the cell on one or more of the eight component strips.

3.7.2 Etched CdS Films

As mentioned in Section 3.6 it was not possible to use patterned photoresist films alone in the standard processing of thin film $\text{Cu}_2\text{S}/\text{CdS}$ cells. The resist will not adequately mask against a 7 second etch of the CdS in HCl at 45°C . Masking was provided for etch durations of about 3 seconds, however. Small area cells were prepared on CdS films masked and etched in that way. The groups of cells on the same film specimen were immersed in CuCl solution at 100°C for intervals of 1, 3, 6 and 10 seconds analogously to the immersions in 90°C solution used for the unetched cells characterized in Figure 34. With etching and CuCl immersion at a somewhat higher temperature, small area strip cells exhibited the V_{OC} -log I_{SC} behavior shown in Figure 35. In comparison with Figure 34 the most striking aspect of the etched cell behavior was the relative insensitivity to CuCl immersion time greater than 3 seconds. As in the case of unetched CdS films, the shortest immersion time resulted in highest V_{OC} values. Interestingly, there was no strong dependence of I_{SC} , at constant illumination power, on the CuCl immersion time.

With the ability to mask against 7 second, 40°C HCL etching by using Waycoat IC over patterned films of SiO (as described in Section 3.6) it should be possible to study the process parameter sensitivity of small cells produced analogously to large area, state-of-the-art cells. The electrical evaluation methods described in this section should allow sensitive distinction in behavior between closely spaced small cells processed slightly differently. In this way the influences of area variations in CdS film properties and the run-to-run fluctuations encountered in processing large area cells which have hampered such attempts in the past can be avoided.

3.8 Laser Scanned Photocurrent Response of Small Area Film Cells

One of the advantages of small area rectangular cells is the ability, at high magnification, to locate specific structural features with regard to the edges and corners of a cell. This ability has been

Fig. 35 — Photovoltaic characteristics of small, thin film cells produced by varying the immersion time in 100°C CuCl solution during Cu_2S layer preparation on a CdS film etched in 40°C HCl for 3 sec. Immersion times of 10, 6, 3 and 1 sec were used for cells giving curves 1 through 4, respectively.

used to compare high resolution, laser scanned photoresponse and scanning electron micrograph images of a special cell. As a result it is possible to correlate certain structural features of thin film $\text{Cu}_2\text{S}/\text{CdS}$ cells with variations in photocurrent response. Although high resolution photocurrent images have been obtained on state-of-the-art thin film cells, correlation with structural features has been precluded by the topological complexity of the HCl -etched CdS surfaces.* To avoid this problem, a non-etched cell was studied. The cell in question was one produced by a 5 second immersion in CuCl , as discussed in Section 3.7.1.

A photocurrent image of one corner of the cell studied is shown in Figure 36(a). The pattern of response is much better defined and more regular than in the case of a cell formed on a highly etched CdS film.⁺ In addition the nature of the pattern is similar to that produced after KCN etching of wet process Cu_2S layers formed on unetched CdS films (see Figure 8 in Section 3.1.4.2 of this report). It would be reasonable to have higher response associated with perpendicular penetration of Cu_2S down grain boundaries.[#] The edge-on junction geometry so produced would be more favorable for light absorption and subsequent carrier collection than the approximately "planar" junction formed on the exposed grain surface.

After the photocurrent image was taken, the area of study was etched in potassium cyanide solution to remove the Cu_2S layer. An SEM image was produced of the specimen surface (Figure 36(b)) having the same magnification as the photocurrent image. Details of image production by the two methods differ; the SEM view is a mirror image of the photocurrent one. It has been possible to correlate most of the high photo-response elements with those of the grain boundaries revealed by etching.

* See Section 3.4 of Reference 9.

+ See Figure 10 of Reference 9.

It should be noted that in the response image of Figure 36(a), the ratio of photocurrent for light and dark regions of the active cell is at most a factor of about 2. The image intensity is not linearly related to current response.

(a)

(b)

Figure 36. Comparison of (a) laser-scanned photocurrent and (b) SEM images of the same region of a $\text{Cu}_2\text{S}/\text{CdS}$ thin film cell. The SEM view is a mirror image of photocurrent one and was taken after etch removal of the Cu_2S layer to delineate CdS boundaries.

The SEM image, of course, contains more fine detail than does the photocurrent image. Some details do not correlate, presumably as a result of photocurrent response for laser spot impingement in fissured and contoured regions of the film surface unrelated to the grain boundary pattern. This notwithstanding, the results of Figure 36 are the first instance of major correlation between local photocurrent response and grain boundary structure in CdS thin film cells.

3.9 (ZnCd)S Film Deposition

An evaporation system was associated for deposition of mixed sulfide films. Details of the substrate and source tooling are shown in Figures 37 and 38 respectively. The substrates are mounted on a graphite holder which is heated using cartridge elements. The system has three thermal sources which are independently controlled. A quadrupole mass analyzer probe (UTC 100C) is mounted alongside the sample and within line of sight of the sources. Both the substrate and the analyzer can be shuttered separately. The total rate of deposition can be monitored by a quartz crystal monitor (Sloan 9000) which is open to all the sources.

A number of depositions have been made to check out the system and to allow initial calibration of the sources.

The optical absorption of a number of runs is shown in Figure 39. These depositions did reveal a number of problems which occur when ZnS and CdS are evaporated in this type of system. Due to the lower sticking coefficient of CdS (and to a lesser extent ZnS), and the high vapor pressure associated with Zn and Cd, there is a severe problem associated with background effects on the mass analyzer. Initially, a shield was placed around the QMA head to prevent extraneous indications from the walls and other surfaces and also to decrease the aperture area facing the source. This was felt necessary to reduce the pressure level sensed by the QMA and to prolong the life of the filaments. Initially no attempt was made to cool the shields and a problem developed with a very large residual Zn and Cd signal. This apparently was due to emissions

Figure 37. A view of the underside of the top plate for the (ZnCd)S evaporation system showing the shielded quadrupole mass analyzer probe head (left) adjacent to the graphite substrate mount with a square glass substrate in place. Also shown are separate shutters for the QMA probe (in the open position) and for the substrate (in the closed position).

Figure 38. A view of the triple source (one is in reserve) arrangement for co evaporation of ZnS and CdS to produce (ZnCd)S film. A quartz crystal monitor is shown mounted above the sources.

Curve 713773-A

Fig. 39 -Optical transmission of (ZnCd) S films

from previous depositions on the shield assembly on heating by the QMA filaments. The temporary solution to this was to remove the shielding while the shielding fixture was redesigned to permit cooling.

The sources are reasonably stable over the durations of a run although there are fluctuations in the overall rate during the deposition. This should not be a serious problem for the device since only the outmost layer of the mixed sulfide film near the Cu_2S affects the junction characteristics. However, the net optical transmission of the film would be affected quite strongly. A few thousand angstroms of a small bandgap compound could dominate the optical absorption as a function of wavelength since $(\text{ZnCd})\text{S}$ is a direct bandgap compound. Lack of time prevented more extensive characterizations of the deposited films.

4. PLAN FOR THE NEXT PERIOD

An analysis of costs will be made for state-of-the-art cell fabrication. A draft of the final report will be prepared, submitted for approval and distributed.

5. ACKNOWLEDGMENTS

The authors gratefully acknowledge the following individuals for contributions to work performed and reported during this quarter: P. E. Barbarich for technical support in specialized cell fabrication, R. A. Hoffman and B. A. Blankenship for metal and oxide depositions, T. A. Temofonte for masks used in photolithographic processing, J. C. Neidigh for photoresist services, C. W. Hughes and T. J. Mullin for SEM characterizations, K. B. Haun for typing and S. Farukhi for editing the manuscript and arranging production of the document.

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