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**CADMIUM SULFIDE/COPPER SULFIDE HETEROJUNCTION
CELL RESEARCH**

Technical Progress Report No. 3, April 1—June 30, 1978

By

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August 23, 1978

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Westinghouse Electric Corporation
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August 23, 1978

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ABSTRACT

Extensive studies have been made of the structural details of Cu_2S films on evaporated polycrystalline CdS layers. Examinations of free standing films reveal Cu_2S penetration along grain boundaries of at least $5\text{ }\mu\text{m}$ on unetched CdS films and of $10\text{ }\mu\text{m}$ or more on etched films. Preliminary structural comparisons have been made on films yielding low ($< 3\%$) and higher efficiency ($\sim 5\%$) cells.

Minority carrier diffusion length values of about $0.3\text{ }\mu\text{m}$ have been obtained from photocurrent response to a laser spot scanned along a Cu_2S layer of graded thickness. Doubling the time of exposure to a 200°C nitrogen ambient used in forming the Cu_2S layer does not significantly change the diffusion length. Anomalously high values of diffusion length ($\sim 1\text{ }\mu\text{m}$) are indicated for a region associated with a crack in the CdS .

Compositional profiling of Cu , S and Cd by ion scattering spectroscopy (ISS) and Auger electron spectroscopy (AES) have yielded generally similar results for Cu_2S films prepared on single crystal CdS substrates. Somewhat greater detail appears in certain of the profiles obtained with ISS which is attributed to less influence of depth averaging than in the AES case.

1. SUMMARY

During the third quarter of this program, significant technical achievements have been realized in three areas of importance to a better understanding of $\text{Cu}_2\text{S}/\text{CdS}$ solar cells: (1) It has been possible to delineate the topography of Cu_2S layers in state-of-the-art cells, with particular emphasis on the $\text{Cu}_2\text{S}/\text{CdS}$ interfacial region. Initial phases of this work were based on an unconventional approach to produce free standing films of Cu_2S by dissolving away the CdS substrate. Cu_2S penetration to depths in excess of $10\text{ }\mu\text{m}$ in grain boundary regions has been revealed. (2) Films of Cu_2S of graded thickness have been prepared on single crystal substrates by utilizing the penumbra effect which occurs on evaporation past a straight edge. Scanned laser spot photoresponse of the resulting structure has produced results agreeing generally with theory and indicating an electron diffusion length of approximately $0.3\text{ }\mu\text{m}$ in the Cu_2S layers studied. (3) Ion scattering spectroscopy (ISS) and Auger electron spectroscopy (AES) have been used at the Pennsylvania State University to produce compositional profiles of Cu_2S layers on single crystal substrates. Correlation of results suggests that the methods should be reliable for characterizing potential compositional changes related to processing influences or degradation phenomena.

Cell fabrication methods have been improved over the course of the quarter with the impact being made primarily in terms of a higher yield of usable cells. Maximum efficiency obtained during the period was 5.5%, with low values of short circuit current and fill factor being the major limitations to better performance. Equipment has been prepared for thermal evaporation of $(\text{Zn}_x\text{Cd}_{1-x})\text{S}$ to permit preparation of films of at least $10\text{ }\mu\text{m}$ thickness for electrical, structural and compositional comparisons with state-of-the-art CdS films. The apparatus accommodates a quadrupole mass analyzer probe which will

permit monitoring and controlling the Zn and Cd specie fluxes in the evaporant stream.

One unexpected result during the quarter was the indication of very high diffusion length values ($\sim 1 \mu\text{m}$) for an extended area ($200 \mu\text{m} \times 1400 \mu\text{m}$) of Cu_2S on single crystal CdS. The region of high photocurrent response (quantum efficiency $\sim 80\%$) was associated with a crack in the CdS substrate. X-ray topography did not reveal effects of the crack, although features associated with the strain gradient produced by a tapered Cu_2S film are prominent.

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 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.

In the discussion of progress on the program which follows, individual technical topics may be referred back to these tasks.

During the first six months of work on this program, effort was applied to reactivating a facility for the preparation of large area thin film $\text{Cu}_2\text{S}/\text{CdS}$ solar cells. Difficulties were encountered initially in obtaining good adhesion of CdS films over the 18 cm^2 zinc plated copper foil substrates.⁽¹⁾ Studies related to film cell performance and mechanisms are based on the availability of such films for the program work. The adhesion problems have been resolved.⁽²⁾

Reacquisition of processing capability for preparing state-of-the-art cells has progressed with steady improvement of cell performance to the point of yielding average conversion efficiency values of 4.8% for cells of 4 cm^2 area.* Local defects have been a problem in permitting achievement of higher performance. The role played by local defects in the CdS layer is magnified by the surface texturing process prior to formation of the Cu_2S absorbing layer. Preliminary work has shown that substrate conditions also influence etching behavior thought to be associated with grain boundaries. Thus, defects and etching behavior are considered very important in the work on the current program to better understand physical mechanisms controlling the behavior of thin film cells.

The use of single crystal CdS substrates has been pursued to eliminate effects, such as defects or mechanisms associated with CdS grain boundaries. Simplified cell structures have been prepared⁺ which are suitable for detailed electrical and optical evaluations. To minimize uncontrolled variations from run to run in Cu_2S formation for such structures, methods of preparing Cu_2S layers of varying thickness on a single substrate have been considered. The vacuum evaporation of CuCl onto a CdS substrate, with subsequent heat treatment to form the Cu_2S layer, is a good method for varying film thickness. To date, films of two thickness values have been produced by moving a shutter after half the desired thickness of CuCl has been deposited on a substrate. The resulting Cu_2S film exhibited photocurrent response to a small area

* Ref. 2, Table II.

⁺ Ref. 1, Section 3.5.

scanned laser spot indicating the expected influence of film thickness on minority carrier photocurrent collection in the cell structure.*

The ability to relate spatial details of photocurrent response to geometric and process related features in single crystal cells establishes the potential importance of this method in the current program for understanding photovoltaic mechanisms in $\text{Cu}_2\text{S}/\text{CdS}$ and $\text{Cu}_2\text{S}/(\text{Zn}_x\text{Cd}_{1-x})\text{S}$ solar cells. Adaptation of the method to cells produced on non-textured CdS films should lead to a much better understanding of mechanisms in state-of-the-art cells.

2.3 Emphasis for this Quarter

The most promising aspects of the technical status resulting from efforts during the first six months of the program, as highlighted in Section 2.1, have been pursued during the present quarter (April 1, 1978 to June 30, 1978). These relate primarily to Tasks 1, 2, 3, 5 and 5 (in Section 2.2). Work on other tasks, e.g., on $\text{Cu}_2\text{S}/\text{Zn}_x\text{Cd}_{1-x}\text{S}$ studies and on improved cells, has begun but efforts have been confined to readying equipment or preparing new mask designs.

Studies of the topography of the $\text{Cu}_2\text{S}/\text{CdS}$ interface in thin film cell structures have been made (Section 3.1). This adds a new capability to characterize, visualize and model this important aspect of state-of-the-art cells. It has been possible because of breakthroughs in exploiting selective etch methods for the materials of thin-film cells. The continued improvement, related to better control and reproducibility of the various processing steps, in thin film cell performance over the quarter is reported in Section 3.2.

A novel method for producing tapered thickness in layers of Cu_2S on single crystal CdS cells is described in Section 3.3. This permits use of scanned laser spot characterization of photocurrent response and of local optical behavior (transmission and reflection) of the test structure to be applied to evaluating influences of Cu_2S

* Ref. 2, Fig. 11a.

thickness in a single cell structure ranging continuously from 0 to 1.5 μm . Description of the equipment, which includes a quadrupole mass analyzer, being readied for (ZnCd)S film evaporation is given in Section 3.4. The use of ion scattering and Auger electron spectroscopy, at the Pennsylvania State University, to obtain compositional and impurity profiles is described in Section 3.5.

3. PROGRAM PROGRESS

3.1 Topographical Studies of Cu₂S/CdS Film Structures

3.1.1 Selective Etching

During this period work was carried out in separating the Cu₂S layer from the CdS film by gently etching away the latter. This is a new technique, there being no accounts in the literature of its being attempted previously. The extreme thinness and presumed fragility of the Cu₂S layer probably discouraged such attempts. It was indeed found that the Cu₂S layer is very thin and fragile, yet with care and special procedures Cu₂S films have been separated from CdS substrates more or less intact. It has been possible to examine the separated layer structure in the scanning electron microscope. Preliminary observations have been carried out on the Cu₂S layer structure of variously processed Cu₂S/CdS thin film solar cells and it is felt that the method could be valuable in guiding efforts to improve cell design and maximize performance.

The key to separating the Cu₂S layer without physically destroying it is the very slow dissolution of the CdS, about 25Å/sec. This has been done on Westinghouse films using a 1:2 HCl to H₂O solution at room temperature. Cadmium sulfide films, about 30 μm thick, produced on the program have been dissolved away in 3 1/2 to 4 hours, leaving the Cu₂S structures intact.

Three variations in details of the technique have been tried: (1) undercutting the CdS film at the substrate interface and dissolving away the CdS until the Cu₂S layer floats free; (2) cementing the Cu₂S surface of a cell to a glass slide, peeling back the substrate, and then dissolving away the CdS; (3) potting and cross-sectioning a cell and then dissolving several microns of CdS from the exposed surface.

3.1.2 Structural Perspectives for Similar Samples

For results reported in this section two of the three methods of preparing samples just discussed were applied to different sections from the same cell ($\eta \sim 5.2\%$). The epoxy replication method was applied to a sample with somewhat lower efficiency, but this is not considered to be important for the purposes of the example. As will be seen, use of the three methods gives different perspectives of the topological configuration of thin film $\text{Cu}_2\text{S}/\text{CdS}$ cells.

The simplest method is to immerse a small section of a $\text{Cu}_2\text{S}/\text{CdS}$ film cell (samples as large as 5 x 20 mm in area have been successfully tried) in a shallow dish containing the HCl solution and to let it stand for about 4 hours. It was observed that the HCl attacks the zinc plating of the substrate much more rapidly than it does the CdS, so that the $\text{Cu}_2\text{S}/\text{CdS}$ film strips off the substrate after a short time. After about 3 1/2 hours the CdS usually seems to be completely dissolved and the residual Cu_2S layer (which is not noticeably attacked by the HCl) floats freely in the solution. At this stage the freed Cu_2S film has a reasonable degree of physical integrity* and with care can be picked up on a glass slide or on a specimen grid. It can then be rinsed, dried, and examined.

Fig. 1a is an SEM view of the bottom surface (i.e., that from which the CdS was etched away) of a Cu_2S layer separated in this way from the textured CdS film of a 5.2% efficient cell. Fig. 1b is a part of the same sample at ten times greater magnification. Some breakage of the Cu_2S is suggested here, presumably as a result of handling. Fig. 2 shows a sample from the same cell etched at another time. The protrusions or columns of Cu_2S are not as densely spaced here (as compared to Fig. 1a). It is thought this is because a large fraction ($\sim 50\%$) of the Cu_2S layer broke away as small local areas during sample preparation, thus leaving

*The strength of the free Cu_2S layer is probably derived from its complex structure, as revealed in Fig. 1, which is loosely analogous to that of honeycomb structural panels.

(a)

(b)

Fig. 1 - The underside (i.e., $\text{Cu}_2\text{S}/\text{CdS}$ interface region) of a free-standing copper sulfide film. [Sample #1, HCl texturing, 5.2% cell.] (a) General SEM view, (b) View at 10 times greater magnification of the boxed region in (a).

Fig. 2 - SEM view of a Cu_2S specimen from the same cell as that shown in Fig. 1, but released from the CdS layer in a separate etching procedure.

fewer Cu_2S "columns" and giving a more open appearance. This facilitates estimating the height of the columns remaining. Some of the columns of Cu_2S in Fig. 2 appear to be about $15\text{ }\mu\text{m}$ in height (implying penetration of this amount from the surface of the original CdS film). For other samples, heights up to about $20\text{ }\mu\text{m}$ were estimated by such observations.

A second technique for separating the Cu_2S layer from the host CdS film is to cement the Cu_2S surface of a cell to a glass slide using epoxy resin and to delaminate the substrate from the CdS layer by physical peeling. Then the CdS can be dissolved in HCl solution as before, leaving the Cu_2S structure cemented to the glass slide. Fig. 3 shows two views at different magnifications of a sample prepared this way, using the same cell as in all the previous cases. The columns of Cu_2S in Fig. 3a are densely spaced, as in Fig. 1a, but there appears to be little breakage of the tops of the columns. The dissolution of the CdS on this sample was stopped after 3 hours leaving some CdS at the base of the columnar structure. This was confirmed by the energy dispersive X-ray analysis attachment (EDAX) to the SEM. (There was no residual CdS detected on the other samples described earlier.) Termination of etching of the CdS just short of complete removal appears to have been effective in retaining the Cu_2S structure intact, without masking the configuration of the Cu_2S from observation.

When cemented samples were etched to completion, the Cu_2S floated free from the adhesive layer and left an epoxy replica of the upper surface of the Cu_2S layer. Fig. 4 shows an SEM photograph of such an epoxy replica. (Compare with bottom surface views in Fig. 1a and 3a at the same scale.) The EDAX showed no Cd, Cu or S present on this sample. The stalagmitic peaks resulted from epoxy resin which penetrated into the holes left from the pre-barrier HCl etch of the CdS film, which for these cells was 7 seconds in 2:1 HCl solution at 45°C . The peaks of epoxy are not as densely spaced as the Cu_2S columns in Figs. 1a and 3a, and it is not clear whether this is because there were not as many etch pit holes in the CdS film as there were major Cu_2S columns (this

(a)

(b)

Fig. 3 - The underside of a Cu_2S film cemented to a glass slide before etch removal of the CdS layer and Cu substrate. Specimen prepared from a textured, 5.2% cell.
 (a) General SEM view, (b) magnified view of the boxed region in (a).

Fig. 4 - Epoxy replica of the outer surface of a Cu_2S layer specimen from a low output (2.6%) CdS thin film solar cell.

sample was from a low output cell), or whether the epoxy resin did not fill all of the holes. It is to be noted that the tallest of these stalagmitic peaks is about 20 μm .

A third technique to delineate the geometric structure of the Cu_2S layer involved potting a portion of a cell in resin, cross-sectioning it through the cell, grinding and polishing the exposed cross-section region to minimize physical damage at the surface, and then dissolving a few micrometers of CdS from the exposed surface in HCl solution, as before, leaving the Cu_2S behind. About 15 to 30 minutes etching in the 1 to 2 HCl solution at room temperature appeared to be optimum for exposing the Cu_2S structure for observation. Longer times resulted in some Cu_2S falling out of place. Fig. 5 is an SEM photograph of a sample of the same 5.2% cell (as the earlier discussed samples) prepared in this way. The arrows indicate the locations of the various layers of the cross-sectioned sample. Except for the zinc-plating, layer identifications were established by EDAX. As in the case of the two previous methods for preparing samples, the zinc layer is etched much faster by the HCl solution. The zinc layer location is indicated by the bounding regions of copper and unetched cadmium sulfide.

The CdS features shown in Fig. 5 are at a much greater depth than the Cu and Cu_2S layers in the cross-sectioned sample. Presumably the structure is due to partial dissolution of individual grains deep in the cross section by the HCl at the end of the dissolution period. Because of the large depth of focus of the SEM views of this type must be interpreted very carefully.

Fig. 6 is a higher magnification view of another portion of the same sample, focussing on the Cu_2S structure. There appear to be two distinct levels of penetration of the Cu_2S in from the original surface of the CdS film. On the basis of this sample and observations on other samples, to be discussed later, it is thought that the more or less continuous Cu_2S structure extending about 3 to 5 μm in from the original CdS film surface may represent Cu_2S which penetrates into grain

Fig. 5 - SEM view of a potted and cross-sectioned 5.2% cell after dissolution of $\sim 5\mu\text{m}$ of CdS from the exposed surface.

Fig. 6 - Another portion of the specimen of Fig. 5 showing enlargement of Cu_2S region.

boundaries from the upper surface of the cell. The columnar structures are thought to be due to Cu_2S which coated the walls of deep etch pits in the CdS film (as in the replica of Fig. 4) and then spread laterally into intersecting grain boundaries.

Figs. 7a and 7b are views at larger magnification of the middle portion of Fig. 6 showing these two distinct regions in more detail. It is not clear if the jagged lower edge of the hollow stalagmite structure of Fig. 7b represents a fracture and loss of the end of the peak, or if it formed at all. It is quite possible that the CuCl solution did not fully penetrate to the bottom of the etch pit--perhaps due to trapped gas during the barrier forming operation.

It is difficult to discern the grain boundary structure of the original CdS film in the views presented in Figs. 6 and 7a. However, Fig. 8 is an SEM photograph of another portion of the same sample where the outlines of the original CdS grain boundaries can be discerned more clearly. Two separate grains, each approximately $1\text{ }\mu\text{m}$ across can be seen in the middle of the photograph while portions of two other grains can be seen on either side. The more or less pyramidal tops of the grains can be seen also. It may be noteworthy that the Cu_2S in this view is not discontinuous. Several explanations are possible for this. The geometric details of the Cu_2S layer adjacent to the surface produced by cross-sectioning may be distorted by that process. Alternatively, local Cu_2S areas may have dissolved or broken away during dissolution of the CdS in HCl. Thirdly, the Cu_2S layers may have actually been formed in this manner originally, and not been altered during specimen preparation.

In the foregoing studies, emphasis was on exploiting the ability to view the topographical features of the $\text{Cu}_2\text{S}/\text{CdS}$ interface revealed by preferential etching and of the outer Cu_2S surface by replication. For these purposes, the methods have been applied to structures using CdS films capable, on appropriate processing, of yielding cells with conversion efficiency values in excess of 5%. The following major conclusions have

(a)

(b)

Fig. 7 - Higher magnification SEM photos of the middle region of Fig. 6. (a) Upper region, at top surface of cell. Cu_2S thought to have penetrated into CdS grain boundaries from top surface. (b) Lower region, Cu_2S thought to be coating walls of deep etch pits.

Fig. 8 - Exposed cross-section view of Cu_2S showing structure at pyramided surface and in grain boundaries of the specimen of Fig. 5.

been reached:

- o Penetration of Cu_2S layers down grain boundaries to depths in excess of 15 to 20 μm have been observed for texture-etched CdS films.
- o Epoxy replication of the outer Cu_2S surface has revealed approximately conical etch features with penetration depths of 20 μm or more in the CdS of about 30 μm thickness.
- o A comprehensive appreciation of the Cu_2S layer and heterojunction topography requires that several methods of specimen preparation be used, with careful comparison of results.

In the next section, studies are reported on specimens produced from several CdS films. The purpose has been to associate topographical differences with cell performance.

3.1.3 Structural Comparisons

The three methods for isolating and studying the geometrical configuration of the Cu_2S layer of $\text{Cu}_2\text{S}/\text{CdS}$ thin film solar cells should be equally applicable to single crystal solar cells and to mixed Cd-Zn solar cells. However, to date there has been time only for a few preliminary examinations of readily available $\text{Cu}_2\text{S}/\text{CdS}$ thin film cells. It is thought that the methods should be of value in analyzing the differences between high and low output cells, and in characterizing certain results of cell processing parameters in order to optimize the physical structure for higher cell outputs. During this period there have been a few attempts to characterize differences in Cu_2S structure due to differences in cell processing and to relate these to differences in cell performance. It is felt that this approach is yielding new insights into the $\text{Cu}_2\text{S}/\text{CdS}$ thin film solar cell.

Initial studies of the structure of the Cu_2S layer were concerned with the differences between high and low output cells and the effect of etching of the CdS film prior to Cu_2S formation. High output cells (those with conversion efficiencies greater than about 3 to 4%) fabricated in this laboratory are characterized by three types of features. They have a high density of etch pits and a pyramided front surface texture - both of which are introduced during the pre-barrier dip etching operation - and a locally deep penetration of the Cu_2S layer.

Figures 9a and 9b are SEM photographs at two magnifications of a specimen of free-standing Cu_2S separated from a section of the same 5.2% cell as the previous samples as viewed from the upper surface of the cell at an angle of 45° . Figs. 10a and 10b are the same with a 0° tilt.

A number of features of these views are of interest. Fig. 9a shows that the CdS film from which the Cu_2S was formed is arranged in clusters of grains about 10 micrometers across. The topology appears to be an approximate replication of the underlying substrate. The pyramid shapes of individual grains are more evident at the higher magnification of Fig. 9b. The structure is pocked with a high density of etch pits, but these are more evident in the head-on views of Fig. 10. It is interesting that a few of the etch pits are nearly perfect hexagons. The variation in the size and distribution of the etch pits is particularly noteworthy. Earlier experience^{*} indicated that low output cells were characterized by an appreciably lower density of these etch pits and a tendency for them to be clustered rather than uniformly distributed, but SEM photos comparable to the present sequence were not taken.

Figs. 11a and 11b are cross-section views of the Cu_2S layer of one of the present generation low output cells. These views show that there is little deep penetration of the Cu_2S in from the front surface of the cell. Compare these with the higher output cell photograph shown in Fig. 6. The deep penetration of the Cu_2S is limited to about 4 to $5\mu\text{m}$ in Fig. 11.

The SEM specimens treated above, on which the views in Figs. 1 through 11 were obtained, were prepared using texture-etched CdS. Except for the case of Fig. 4, all the specimens were from the same CdS film deposition (#560). Film #560 was a representative film of the present state of the art at Westinghouse. When processed using the standard cell fabrication procedures which include a 7 second pre-etch in 2:1 HCl solution at 45°C and a 6 second dip in concentrated CuCl solution at 100°C , the cells were 4.9 to 5.4% efficient. However, when processed without the HCl pre-etch, the cells were less than 2% efficient.

^{*}Ref. 3, pp. 20-23.

(a)

(b)

Fig. 9 - Upper surface of free-standing Cu_2S layer separated from 5.2% efficient cell formed on textured CdS film. (a) General SEM view. (b) Detailed view at greater magnification of the boxed area in (a).

(a)

(b)

Fig. 10 - Specimen of Fig. 9 using 0° Tilt of electron beam.
 (a) General view. (b) Magnified view of the indicated portion in (a).

(a)

(b)

Fig. 11 - SEM photos of potted and cross-sectioned specimen from a low output (2.8%) cell after dissolution of $\sim 5\mu\text{m}$ of CdS from the exposed surface. Two different regions are shown in (a) and (b).

Fig. 12 shows SEM photographs of the separated Cu_2S layer from that low output cell that had no pre-barrier etch as viewed from the Cu_2S -CdS interface side, and Fig. 13 as viewed from the upper surface of the cell. Figs. 12a and 12b should be compared with Figs. 1a and 1b of a textured cell, while Figs. 13a and 13b should be compared with Figs. 9a and 9b. It is significant that appreciable penetration of the Cu_2S into grain boundaries has occurred from the front surface to estimated depths of 4 to 5 μm even though there was no pre-etch. This is contrary to what had been generally thought until now.

Note the absence of holes in the film of Fig. 13. The smooth shapes at the upper left and lower right-hand corners of Fig. 13a are the specimen grid on which the Cu_2S was lifted and through which the film is being observed. It should be noted also that this film was deposited onto the smooth surface of the electroformed copper foil substrate, rather than onto the mat surface. Thus the topology of the CdS film surface (and hence the upper surface of the Cu_2S) is different and the hillock clusters of grains as in Fig. 9a are not in evidence here. However small protuberances or "growth anomalies" are very evident.

3.2 Cell Fabrication

3.2.1 Overall Performance

With the improved adhesion of CdS films on zinc-plated copper foil substrates, and improved control over particle spattering during CdS film deposition, the efforts to re-acquire the earlier state-of-the-art of Cu_2S /CdS cell fabrication proceeded at a faster rate this quarter. The number of cells fabricated, the yield of usable cells, and the output levels of the usable cells have increased from month to month. Fig. 14 shows graphically how cell output has improved over the period of the contract to date. Also given are the number of usable cells fabricated and the number whose efficiency exceeded 5%.

Table I lists the number of cells fabricated each month, the yield of usable cells and the number of cells rejected in various

(a)

(b)

Fig. 12 - The underside of a free-standing Cu_2S specimen separated from a cell given no texture etching prior to barrier formation. (a) General view, (b) magnified view of the indicated region in (a).

(a)

(b)

Fig. 13 - The upper side of the Cu_2S specimen of Fig. 12.
(Compare with Fig. 9.) (a) General SEM view,
(b) view at 10 times greater magnification of the
boxed region in (a).

Fig. 14 - Progress in cell fabrication on this program in terms of efficiency and yield of cells on a monthly basis.

categories. Table II gives details on cell performance in terms of selected parameters for usable cells. The general trend of improvement over the period is evident, although the levels are still lower than was achieved earlier and that have been achieved at a few other laboratories. The present efforts however have been in effect for a relatively short period at a relatively low scale of operation. Also, the data presented here are on all cells fabricated during the period including those in a number of various experiments with selected changes in film deposition parameters and Cu_2S barrier formation conditions.

It will be noted that the largest cause of cell rejects this period was low current output. This was a direct result of some experimental trials of different pre-barrier dip etch conditions including some that had no pre-etch at all. Those cells fabricated according to the base line process improved substantially in regard to their current output with most of those cells yielding short circuit current densities in the 16 to 20 mA/cm^2 range. The higher current levels followed a return to the stronger HCl pre-barrier etch conditions that had been in use several years ago. These were made practical by the achievement of better CdS film depositions. The increase in the average specific dark shunt resistance is thought to be a direct result of the improved control over quartz wool packing giving less CdS particle spattering during CdS film deposition.

Starting in May, the specific shunt resistance of the cells under illumination has been recorded and reported. This parameter is being taken as the slope of the light I-V characteristic curve as it crosses the current axis. It is felt that the specific light shunt resistance gives a better measure of shunt leakage under actual cell operating conditions. Wide variations have been observed in the ratio of the light to dark specific shunt resistances and an attempt will be made to correlate this ratio with cell fabrication parameters.

TABLE I

YIELDS OF USABLE CELLS - THIRD QUARTER

<u>Month</u>	<u>No. of Cell Starts</u>	<u>Rejected Cells</u>				<u>Yield</u>
		<u>Shorted</u>	<u>Low Current</u>	<u>Other</u>	<u>Total</u>	
April	24	4	4	12	20	17%
May	60	6	23	4	33	45%
June	54	5	16	4	25	54%

TABLE II

AVERAGE VALUES OF SELECTED PARAMETERS FOR USABLE CELLS - THIRD QUARTER

<u>Month</u>	<u>V_{OC} (v)</u>	<u>J_{SC} (mA/cm²)</u>	<u>η(%)</u>	<u>Fill Factor</u>	<u>R[*] series (Ω)</u>	<u>R[*] shunt (Ω)</u>	<u>w/light</u>
April	.460	14.7	4.1	0.60	1.3	370	-
May	.463	16.8	4.5	0.59	1.2	1980	175
June	.451	16.3	4.5	0.61	0.9	1890	226

3.2.2 Barrier Process Variations

The original barrier formation process for obtaining high output $\text{Cu}_2\text{S}/\text{CdS}$ thin film solar cells consisted of a strong HCl pre-etch followed in rapid succession by dipping in hot concentrated CuCl solution, deionized water rinsing, drying in an argon stream and heat treating in an air circulating oven. The critical features were the strength of the HCl pre-etch (composition, time and temperature), maximum concentration of CuCl in the dip solution, and strong agitation during dipping. From time to time it has been necessary to make changes in the pre-etch conditions in order to produce high output cells from the CdS films. The changes in film properties which necessitated these modifications in barrier formation were not identified.

In this period a number of experiments were carried out in an attempt to further elucidate effects on cell behavior due to the pre-etch and the CuCl dip. These experiments showed that better results were obtained on present generation CdS films fabricated in this laboratory if a 5 second etch in 2:1 HCl solution at 45°C was substituted for the 15 second etch in 1:1 HCl solution at 60°C that had been in use. The improvement in cell outputs described in the above section were obtained after this change in conditions, probably being due to improved CdS film deposition procedures which made the stronger pre-etch practical.

In an effort to "fine tune" the barrier processing parameters for maximum cell output, a series of experiments was carried out varying first the barrier dip time and second the pre-etch concentration. Table III summarizes the results of varying the barrier dip time on the finished cell parameters. Varying the dip time would be expected to change the thickness of the Cu_2S layer, with best results being obtained when the Cu_2S layer thickness suitably matches the minority carrier diffusion length in the Cu_2S . Over the range studied no clear trend is evident. Slightly higher average short circuit current and cell efficiency were obtained for the 6 second dip time, and this time has been adopted for the base line process.

TABLE III

EFFECT OF BARRIER DIP TIME ON CELL PARAMETERS

(5 second pre-etch in 2:1 HCl at 45°C)

Cell No.	Barrier Dip Time	V_{OC} (v)	J (mA/cm ²)	η (%)	Fill Factor	R_{series} (Ω)	Dark R_{shunt} (Ω)	Light R_{shunt} (Ω)	"A" Factor		I_o (Amperes)
									Hi V	Low V	
562-5	4 sec.	.470	19.5	5.3	0.58	0.9	1250	148	1.6	2.5	2×10^{-5}
-6	"	.465	18.0	4.7	0.56	0.7	1200	140	2.0	2.3	1.5×10^{-5}
-9	5 sec.	.450	13.5	4.6	0.59	1.1	1470	162	1.0	2.6	4×10^{-5}
-12	"	.455	16.9	4.7	0.64	1.0	1750	168	1.1	2.3	1×10^{-5}
-7	6 sec.	.455	19.5	5.3	0.60	0.9	640	144	1.5	2.5	2×10^{-5}
-8	"	.460	19.0	5.2	0.59	1.0	728	152	1.2	2.5	3×10^{-5}

In another experiment a series of cells were processed using a weaker and a stronger HCl pre-barrier etch. The base line process uses a 2:1 HCl to water etch for 5 seconds at 45°C. For this series this etch was compared with a 3:2 and a 3:1 HCl concentration etch. From this experiment there appeared a strong trend towards higher A (diode ideality) factors and higher reverse saturation currents with increasing concentration of the etchant. This is shown in Table IV.

The cell currents from this series were somewhat lower than normally experienced for base line process cells, which resulted in lower cell efficiencies. This is tentatively attributed to some unexplained characteristic of the CdS film from which these cells were made, which resulted in the appreciably less penetration of the Cu₂S layer (during barrier formation) than normal. This difference is discussed in Section 3.1.3 and is illustrated in Figs. 6 and 11. However, the apparent correlation of one of the major cell processing steps with two of the basic cell parameters could be very significant and lead to a better understanding of the operation of the cell and eventually to higher outputs. Further work along these lines is planned for the next period.

TABLE IV

EFFECT OF ETCH CONCENTRATION ON BASIC CELL PARAMETERS

(5 second etch at 45°C followed by 6 second barrier dip at 100°C)

Cell No.	HCl:H ₂ O	Diode Ideality Factor		Reverse Saturation Current (amp)
		High V Range	Low V Range	
563-1	3:2	1.3	2.3	6 x 10 ⁻⁶
-8	3:2	1.0	2.0	2 x 10 ⁻⁶
-4	2:1	1.2	2.8	1.5 x 10 ⁻⁵
-5	2:1	1.3	2.8	2 x 10 ⁻⁵
-2	3:1	1.5	3.2	1 x 10 ⁻⁴
-7	3:1	1.4	3.5	0.9 x 10 ⁻⁴

3.3 Minority Carrier Diffusion Length Evaluation in Cu_2S Films

3.3.1 Preparing a Cu_2S Film with Tapered Thickness

In the preceding quarterly report on this program, successful efforts were described for the formation of Cu_2S layers of stepped thickness on a single crystal substrate.⁽²⁾ The thickness step was produced by moving a mechanical shutter over the substrate part way through the evaporation of CuCl , producing two different thicknesses of this precursor material for Cu_2S . Heat treatment is required to yield the desired sulfide on penetration of the Cu and exchange with cadmium.

Instead of a stepped layer of Cu_2S , it is more desirable to deal with a layer which is approximately linearly graded in thickness. In this way a structure is produced analogous to a conventional bevelled junction for which photocurrent response as a function of light spot position should yield minority carrier diffusion length in a straightforward manner.⁽⁴⁾ One means considered for obtaining the desired linear taper involved evaporation past a shutter moving at constant velocity. Costly and complex to implement, this method was not pursued beyond the stage of concept. Furthermore, each element along the tapered region could, in principle, be produced under slightly different evaporation conditions, thus introducing some uncertainty in the validity of experimental results.

Natural tapering in thickness of an evaporated layer occurs near the edge of an aperture mask not in intimate contact with the substrate. This penumbra effect is often an undesirable feature of thin film processes. Considerable attention may be focussed on controlling the geometry of the system (i.e., evaporant source size, source to substrate spacing and mask to substrate spacing tolerances) to minimize this penumbra effect. In the present case, it can be used to advantage. The thickness profile of an evaporated CuCl layer in the vicinity of a mask edge produced in this way on a polished CdS single crystal substrate is shown in Fig. 14. Source-to-substrate and mask-to-substrate spacings were about 25 cm and 0.5 cm, respectively. A silicon monoxide baffled evaporation source was used.

Fig. 15 - Thickness profile of a CuCl layer evaporated past a mask edge.

Measurements of Cu_2S layers formed after a standard nitrogen heat treatment (200°C , 10 min) and rinsed with methanol and water indicate a CuCl to Cu_2S thickness conversion ratio of about 3 to 1.* On this basis the CuCl profile of Fig. 15 could be transformed into an equivalent Cu_2S layer thickness profile, for standard heat treatment. Measurements of Cu_2S layer thickness for such tapered arrangements have been made by profiling the depression resulting from preferential etching of the Cu_2S with potassium cyanide. Such an approach is undesirable in that it involves sacrifice of the tapered cell structure and precludes its further use.

Instead of measurement of the physical thickness of the Cu_2S layer, the completed device structure can be mounted and subjected to optical evaluation in terms of local transmission and reflection along the length of the taper. Done in this way, with the same He-Ne laser spot as for photocurrent evaluation, the absorption behavior of the Cu_2S layer along the taper can be determined. Effective optical thickness of the Cu_2S film can then be inferred.

3.3.2 Typical Experimental Results

A sample was made by preparing on a polished CdS substrate a Cu_2S layer of tapered thickness as described above. Under the condition used, the tapered region was formed over a distance of 1.5 to 2 mm. The Cu_2S layer thickness varied from a few hundred Angstroms (due to scatter of the evaporant stream) to a value of 2 to 3 micrometers.

Typical results of laser scans along the length of the tapered Cu_2S region are shown in Figs. 16a, b, c for collected photocurrent, optical transmission through the sample and intensity of light reflected from the air/ Cu_2S interface. The latter two parameters are measured by using a photocell detector.

* On the basis of density, a conversion ratio of 2 to 1 is expected. The difference implies that in addition to the sulfide formation, sinks for copper exist in this process of Cu_2S preparation.

(a)

(b)

(c)

Fig. 16 - Electrical and optical behavior for a tapered Cu_2S film on single crystal CdS using a scanned laser ($6330\text{\AA}$) spot. Response from the constant thickness ($\sim 2.5\text{ }\mu\text{m}$) region is at the left in each case. (a) Collected photocurrent, (b) transmission, (c) reflected light. [Vertical scales, in arbitrary units; horizontal scale, $\sim 200\text{ }\mu\text{m}/\text{maj. div.}$]

The photocurrent response of Fig. 16a is relatively uncomplicated. Low uniform response at the left is for the full thickness of the Cu_2S layer, beyond the penumbra region of the CuCl deposition. Photocurrent rises to a peak since a greater fraction of carriers (generated within $\sim 0.3 \mu\text{m}$ of the air/ Cu_2S interface) reach the collecting barrier of the heterojunction as the Cu_2S film thickness is reduced. With further reduction of thickness, the current falls due to increased surface recombination influence and lower total absorption within the Cu_2S film. The local reduction of photocurrent just to the right of the peak is large in amplitude ($\sim 30\%$) and must be attributed to a local electronic effort having influence on a region of 75 to 80 μm in width. This is inferred from the lack of a transmission feature of this part of the scan (Fig. 16b).

As implied in Section 3.3.1, data of the type given in Figs. 16b and c can be used to infer the optical thickness of the Cu_2S layer along the scan line. The ratio, T , of transmitted incident light for a film of thickness t is given by

$$T = (1-R_1)(1-R_2)(1-R_3)e^{-\alpha T}$$

R_1 , R_2 and R_3 are the respective values of reflectivity at the air/ Cu_2S , $\text{Cu}_2\text{S}/\text{CdS}$ and CdS/air interfaces. No absorption in the CdS is considered; α is the value of absorption coefficient of the Cu_2S . The value of R_1 as a function of position can be determined from Fig. 15c. In this regard, the decrease of reflectivity from the value for Cu_2S (28% in the case of the pure material) to that for CdS ($\sim 18\%$) over the large distance ($\sim 1 \text{ mm}$) is unexplained at this time. Change over a very short distance is expected for the simplest case. The other two reflectivity terms are assumed to be constant, and are calculated on the basis of known values of indices of refraction. Thus, the transmission information of Fig. 16b can be transformed to give optical thickness of the Cu_2S as a function of position along the scan line.

When the photocurrent data of Fig. 16a is plotted as a function of equivalent Cu_2S layer thickness, the upper curve of Fig. 17 results. The lower curve is for the same type of evaluation after an additional 10 min at 200°C heat treatment in nitrogen. This involves doubling the time of exposure in the original heat treatment for Cu_2S layer formation. Implications of the two curves are treated in terms of the theoretical discussion of the next section.

3.3.3 Theory and Interpretation

Mulder has developed a theory applicable to the present case.⁽⁵⁾ Surface recombination velocity, minority carrier diffusion length and optical absorption coefficient are parameters in an expression giving collected photocurrent as a function of Cu_2S layer thickness. Monochromatic excitation is assumed. As originally applied the theory was used to treat data for $\text{Cu}_2\text{S}/\text{CdS}$ structures of uniform Cu_2S layer thickness. Comparisons of photocurrent response at two different wavelengths were made to deduce values of minority carrier diffusion length. Values of 200 to $300\text{\AA}$ were inferred for chalcosite specimens.

As applied to the present case, Mulder's formulation of predicted photocurrent response gives the curves shown in Fig. 18. An increase in S , the surface recombination velocity, reduces the peak current response and requires a somewhat greater thickness of Cu_2S to give peak response. For thin layers, surface effects are predicted to reduce response by $\sim 50\%$ (for $S \rightarrow \infty$ in comparison to $S = 0$). For films thicker than about twice the diffusion length, this influence is less, giving at most about a 25% reduction and decreasing for greater thickness values.

Conventional use of a bevelled junction structure for evaluation of minority carrier diffusion length usually involves treating data in the region for which photocurrent response falls off exponentially with distance. For $S \rightarrow \infty$, this situation is not achieved until very large thickness values ($x \gtrsim 10l$) are considered. If the slope of a response curve is used to estimate diffusion length without meeting this

Fig. 17 - Photocurrent response to a scanned laser spot (6330Å excitation) of a cell structure having a CdS layer of graded thickness. Upper curve: Cu₂S layer given a base-line heat treatment in N₂ for 10 min at 200°C. Lower curve: after an additional 10 min, 200°C treatment in N₂.

Fig. 18 - Theoretical curves of photocurrent response as a function of thickness of the illuminated absorber layer in a $\text{Cu}_2\text{S}/\text{CdS}$ solar cell for limiting and intermediate surface recombination velocity values.

requirement, the estimate will be somewhat high. Consideration of families of curves covering ranges of film thickness and diffusion length, and of the analytic form of the response function can allow estimation of the difference between actual and indicated values for the diffusion length.

In light of these considerations, the experimental results of Fig. 17 can be viewed against the theory. For the upper curve, the thickness for peak response occurs at about $0.6\text{ }\mu\text{m}$. If infinite surface recombination velocity were to obtain, a value of L of about $0.4\text{ }\mu\text{m}$ ($2/3$ of $0.6\text{ }\mu\text{m}$) would then be indicated. Evaluation of the slope at a thickness of about $1.2\text{ }\mu\text{m}$, after correction for the reasons discussed above, yields an estimate for diffusion length of about $0.37\text{ }\mu\text{m}$.

Neither the position of the peak nor the slope at greater Cu_2S layer thicknesses of the lower curve is affected by the extra heat treatment. This indicates that minority carrier transport has been unaffected. Since a very high value of surface recombination velocity was assumed in treating the upper curve, the suppression of photocurrent by the heat treatment is attributed to changes in the collection efficiency of the heterojunction barrier itself. Additional modelling will be necessary to elucidate such influences.

The effect of a white bias light on the sample response is shown in Fig. 19. There is an increase in the photocurrent in the surface dominated portion of the curve for small thickness values. This increase could be caused by a photo-dependent light modulation of the surface recombination behavior, or of the junction collection efficiency. The latter seems more likely to explain the loss of enhancement for Cu_2S layer thickness in excess of about $0.9\text{ }\mu\text{m}$. At such a thickness there would be insufficient light intensity at the junction to affect collection mechanisms.

3.3.4 Anomalous Local Photocurrent Response

In the course of scanned laser studies on tapered films of Cu_2S on single crystal CdS substrates, a specimen was found with an

Fig. 19 - Bias light enhancement of photocurrent response from the thinner part of a tapered Cu_2S layer.

anomalously high photocurrent response in an area of thick Cu_2S . A photocurrent image of this region is shown in Fig. 20a, with the single line scan (taken just below the middle of Fig. 20a) of Fig. 20b giving details of the response amplitude. There is no indication of any correlatable features in the transmission image (Fig. 21a) or a detailed single scan of transmitted light amplitude (Fig. 21b) of the area in question. This rules out the possibility of a thinned region of the Cu_2S layer (due to a scratch) giving a higher response. In the reflection mode image of Fig. 20c, several long features are visible. One of these is associated with the enhanced photocurrent response.

An estimate was made of the internal quantum efficiency associated with the anomalous response, yielding a value of about 80%. This requires an exceptionally high value for the diffusion length of electrons in the Cu_2S layer ($\sim 1 \mu\text{m}$) to account for the observations, assuming the high response region is comparable in thickness to that of the surrounding film. One hypothesis for the enhanced response is that the CdS material in the vicinity of the long, scratch-like feature in Fig. 17c is strained, affecting the properties of the Cu_2S formed thereon in such a way that a higher electron lifetime results.

SEM and X-ray microprobe analyses were made of the highly responsive and adjacent areas. In the micrographs, the defect appears as a crack, rather than a scratch. The X-ray results suggest that the area of strong photocurrent response is slightly deficient in copper by about 5%, in comparison with nearby material of lower response. Additional studies are needed to substantiate these findings and incorporate them in an acceptable model for the phenomenon.

X-ray topographs were taken of the sample, but it was not possible to produce an image with details specific to the region of anomalous photocurrent response. A topograph of the entire sample ($\sim 0.5 \text{ cm} \times 0.5 \text{ cm}$ in overall size) is given in Fig. 22, showing several types of features, the most prominent of which are low angle grain boundaries (white, vein-like features). Scratches to the right

(a)

(c)

(b)

Fig. 20 - Anomalous photocurrent response from a thick ($\sim 3 \mu\text{m}$) layer of Cu_2S on single crystal CdS . (a) Photocurrent image ($\sim 200 \mu\text{m}/\text{maj. division}$). (b) Photocurrent amplitude (arbitrary vertical scale) for a horizontal line scan just below the middle of (a). (c) Reflection image corresponding to (a).

(a)

(b)

Fig. 21 - Transmission image (a) and line scan (b) corresponding to the photocurrent image and line scan of Fig. 17a and b, respectively.

Fig. 22 - X-ray topograph of a single crystal CdS substrate having a Cu₂S layer of graded thickness (thickest part [$\sim 3 \mu\text{m}$] at far left).

of center in the figure are a result of probe contacting for electrical evaluation. The region of the Cu_2S layer appears in the left part of the figure, with the thickest portion at the far left. No direct response of the Cu_2S layer is shown; however its presence is associated with the network of dark vertical lines in the left third of the image. Some of these are associated with low angle grain boundaries. A suggested explanation is that the dark lines reflect strain associated with lattice mismatch between the Cu_2S layer and CdS substrate.

3.4 Thermal Evaporation System for $(\text{Zn}_x\text{Cd}_{1-x})\text{S}$ Films

Initial experiments on the formation of thin films of mixed $(\text{ZnCd})\text{S}$, using electron beam deposition techniques, yielded films whose compositions corresponded quite well to the composition of the source material. However the available equipment lacked sufficient capacity to deposit films with thickness ($> 10 \mu\text{m}$) suitable for state-of-the-art solar cells. In addition, the EB equipment does not allow flexibility in controlling the doping and stoichiometry of films. This is easier to implement if separate thermal sources are used. In order to monitor and control the composition of the evaporant stream, a deposition system was designed for controlled evaporation of CdS and ZnS. This system will be fitted with a quadrupole mass analyzer (QMA) and a quartz crystal rate monitor. This system is shown in Fig. 23.

The QMA is a model UTI 100C, having a mass range of 1 to 300 AMU. The detector is placed so as to intercept a portion of the flux from each of the sources and thus can be used to monitor the rate of arrivals of the various species incident on the substrate.

The overall rate will be monitored by a quartz crystal monitor and controller (Sloan 9000). This sensor is open to all three sources, however, it is aimed preferentially at the CdS source. The output from this unit will be used to control the CdS source to a preset rate. The QMA will be used to control the ZnS source initially and later to control the third source, which can be the dopant for the $(\text{CdZn})\text{S}$.

Fig. 23 - System for Thermal Evaporation of $(Zr_xCd_{1-x})S$ Films Including Quadrupole Mass Analyzer Probe.

3.5 Compositional Profiling

Work has been done at the Pennsylvania State University to evaluate compositional profiles in $\text{Cu}_2\text{S}/(\text{single crystal}) \text{ CdS}$ structures using Auger Electron Spectroscopy (AES) and Ion Scattering Spectroscopy (ISS). Both methods have good sensitivity and resolution for the major chemical constituents of the cell structures. Since both electron and ion beams are used for these characterizations, the opportunity exists to detect effects, if any, of the beams on the specimens themselves.

3.5.1 Sample Preparation

The single crystal CdS used in this work was 10 ohm-cm, Cl-doped, C-axis oriented material obtained from Eagle-Picher. Die of $\sim 15 \times 15 \times 0.5$ mm dimensions were cut from the boule. Ohmic contacts were formed by the sequential evaporation of indium ($\sim 500\text{\AA}$) and aluminum ($\sim 500\text{\AA}$). No heat treatment was used in the ohmic contact formation.

A simple lacquer film mask was used to define cells on the front surface and to cover the sides and ohmic contact. To form the cell, the front surface was etched with a 3:1 solution of hydrochloric acid and deionized water. There was no rinse of the etching solution prior to immersing the die in a boiling saturated solution of CuCl in deionized water. A thin p-type Cu_2S layer was obtained for a dipping time of 10 seconds. The mask was then removed with acetone. For some devices a Cu layer (30-150 $\text{\AA}$ thick) was evaporated onto the Cu_2S surface. Front contacts were made to the Cu- Cu_2S or Cu_2S layers by gold evaporation. Electrical measurements were performed before any subsequent heat treatment.

3.5.2 Results

Ion scattering spectroscopy (ISS) was used to measure the composition versus depth profile of the cells. The probe beam (Ne-20 at an energy of 1.1 keV) was scanned with sampling done on a $250 \mu\text{m} \times 1000 \mu\text{m}$ area. The ISS depth scale was estimated from an average

sputtering rate of about 10Å/min. Auger electron spectrometry (AES) also was used to profile the composition, with 3 keV electrons. The sampled region of the AES scan was 250 µm in diameter with a depth defined by the Auger electron escape depth. Typical Auger electron escape depths are Cu - 15Å; O - 11Å; Cd - 10Å; Cl - 7Å; and S - 6Å. Two regions of the same size on a typical die were scanned using ISS and AES. Spot #1 represented a region without electrode metallization, while Spot #2 overlapped two Au contact fingers of the electroded cell.

For Spot #1 the ISS composition versus depth profile is shown in Fig. 24a. The surface was copper rich due to the copper deposition used for this particular cell. A graded copper region extended up to ~ 450Å from the surface. At this depth an approximately constant Cu/S ratio of 1.1 was noted. Fig. 24b shows the AES data from the center of the area bombarded by the ion beam in ISS. The following are noted:

- (1) The enrichment of copper at the surface is not as obvious as in the ISS analysis primarily because the AES signal is averaged over ~ 15Å from the surface.
- (2) The surface is also sulfur deficient, in agreement with the ISS data; at t = 50 min., trends in the Cd and Cu signals obtained by ISS and AES were similar.
- (3) The chlorine signal detected with AES was ~ 1.7% of the sulfur signal and seem to follow the latter at t = 100 min.
- (4) The oxygen detected by AES completely disappeared at t = 130 min., on exposure of the CdS substrate. The signal level was ~ 0.5% of the sulfur peak at t = 64 min.
- (5) Carbon completely disappeared at t = 96 min. Signal levels were also low.

Fig. 25a is the ISS Profile for a sample area between Au contacts (spot #2). This shows that:

- (1) Up to ~ 500Å, the region was rich in Cu.
- (2) The interface was reached at t = 85 min.
- (3) The Cu/S ISS ratio of 1.1 was obtained between t = 38 min. and t = 93 min., or a thickness of about 550Å.

Fig. 24 - Composition and impurity profiles for $\text{Cu}_2\text{S}/\text{CdS}$ specimens for sampling areas beyond the electroded cell structure. (a) ISS data. (b) AES data.

Fig. 25 - Compositional and impurity profiles for $\text{Cu}_2\text{S}/\text{CdS}$ specimens for sampling areas which include gold electrode portions of a cell structure.
(a) ISS data, (b) AES data.

- (4) Beyond $t = 100$ min., a significant increase in the Cu signal was observed by ISS. Note that this increase occurred after detecting Cd. One is tempted to conclude that copper may have diffused inward from the surface after testing because of the lower initial ISS copper signals. However, it must be stressed that the area sampled by ISS here may not be equivalent to that in spot #1 because of the presence of Au contacts surrounding Spot #2.
- (5) The dip in the S signal beyond $t = 60$ min. is the same as that obtained in Fig. 21a. Beyond $t = 100$ min., however, notably at the region of the Cu pile-up, trends in the S signals were different. Similar observations hold for Cd.
- (6) The symbols indicated by (AES) show at which times the AES data were obtained. This was done to investigate the effects (if any) of electron bombardment during AES analysis. So far, the data do not indicate any unusual effects.

The number of AES scans on this spot was less because it was decided to optimize the ISS data. The results of the AES scans (Fig. 25b) reveal the following:

- (1) This method appears to be insensitive to the fine details of the Cu signal observed in ISS from $t = 8$ min. to $t = 110$ min. The copper pile-up observed in ISS (Fig. 25a) was also indicated in the AES data point at $t = 175$ min.
- (2) Trends in the sulfur signal were similar to that obtained in Fig. 25a.
- (3) Cadmium was detectable using AES at $t = 100$ min., whereas ISS showed Cd at $t = 85$ min. Note that in AES scan was made at $t = 90$ min. and did not show the Cd.
- (4) Oxygen completely disappeared in the AES profile at $t = 25$ min. but returned at $t = 100$ min. The oxygen signal at $t = 175$ min. is higher than the true value because the AES data was obtained by scanning the S and Cu peaks, then the oxygen one. By the time zero signal was recorded, the sample had already been irradiated with the electron beam for 72 secs. Even so, the oxygen signal was small.

- (5) Chlorine was also detected, but the signal levels were low, as in Fig. 24b.
- (6) Only one carbon peak was obtained at $t = 8.1$ min. because the presence of the Au signal at 277 eV affects the carbon signal at 272 eV.

3.5.3 Comments

The $\text{Cu}_x\text{S}/\text{CdS}$ system is very amenable to study using ISS and AES, because of sufficient sensitivity and resolution for the major elements involved. In particular the peaks of the constituents are well resolved with ISS and can be readily monitored on a computer-controlled profile. Since both ion beams and electron beams are used in this characterization work, the effects of the beams themselves on the samples must not be overlooked. As this heterojunction can be studied by both methods (i.e., ISS and AES), one technique can be used to check the other. These preliminary results presented show that evaporated gold electrode grids can shift the indicated stoichiometry of the Cu_xS layer. The preliminary results suggest that with application of the grid Cu was driven across the Cu_2S layer to the $\text{Cu}_x\text{S}/\text{CdS}$ interface. The source of the Cu is apparently the ultra thin Cu layer evaporated on the Cu_xS .

4. PLAN FOR NEXT QUARTER

During the fourth quarter of this program (July 1, 1978 to September 30, 1978) effort will be applied to all nine tasks listed in Section 2.2. The general emphasis for each task will be as follows:

1. Conclude effort on controlling and evaluating CdS layer properties.
2. Continue efforts to characterize minority carrier transport properties of Cu₂S layers. Explore the possibility of deliberate surface damage to modulate Cu₂S properties. Extend the work to layers formed on polycrystalline CdS films.
3. Conclude prototype cell fabrication and evaluation.
4. Prepare films of (Zn_xCd_{1-x})S by thermal evaporation, using a quadrupole mass analyzer to monitor Zn and Cd fluxes. Begin structural and electronic characterizations of the alloy films for comparison with the CdS case.
5. Model effects of local variations in electrical behavior of film cells for prediction of influences on performance of large area cells.
6. Extend minority diffusion length measurements on heat treated cells to include thin film cells. Utilize small area cell structures to identify local influences on degradation or changes in cell behavior resulting from various heat treatments.
7. Attempt to implement optimized etching conditions to improve cell performance, utilizing a variety of cell sizes if necessary to identify and isolate localized effects.
8. Begin assessment of program findings in terms of implications for improved cell performance.
9. Produce an initial analysis of costs for state-of-the-art cell fabrication using a standardized cost accounting method, similar to that being applied in the area of silicon solar cell modules.

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