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GROWTH AND Cu_xS -(Cd, Zn)S HETEROJUNCTIONS

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RECENT RESULTS ON (Cd,Zn)S SINGLE-CRYSTAL FILM GROWTH

AND $\text{Cu}_x\text{S}-(\text{Cd,Zn})\text{S}$ HETEROJUNCTIONS

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and Development Administration.

I. INTRODUCTION

The Cu_xS -CdS heterojunction employed in the so-called cadmium sulfide solar cell has, until recently, been acknowledged as the only serious competitor of the silicon cell, at least for terrestrial applications. It could be manufactured in thin-film form using vacuum evaporation techniques which were expected to yield substantial cost savings compared to the single-crystal technology apparently required for efficient silicon devices. The large-scale use of the CdS cell has been delayed, however, by at least two major problems: relatively low efficiency and uncertain device lifetime. Ameliorating these two problems has been the object of several research programs both in Europe and the U.S. within the past decade⁽¹⁾. Although there has been some success in these aims, present day cadmium sulfide cells remain less than 10% efficient and and possess no longer than about a 20-year expected life.

Prompted both by the possibility of obtaining a cell without the problems of the CdS cell and the hope of contributing to a more perfect understanding of the Cu_xS -CdS heterojunction, we began an investigation of the Cu_xS -(Cd,Zn)S heterojunction. The addition of ZnS, forming a "mixed crystal", on the n-type side of the junction was expected to have several beneficial effects, including 1) higher open-circuit voltage, meaning higher efficiency, 2) greater stability because of the decreased copper diffusivity in the mixed crystal, and possibly 3) higher short-circuit current because of a better lattice match at the interface. The preliminary results, reported in reference 2 were sufficiently encouraging to warrant a continuation of this program. Therefore, with the aid of a National Science Foundation post-doctoral fellowship, we set out

to study cells of various Cd-Zn ratios.

It was decided to study heterojunctions formed on single-crystal substrates in order to avoid complicating effects of grain boundaries. It was hoped that a supplier of mixed crystals could be found so that our efforts could be concentrated on heterojunction formation and characterization. Although a considerable effort was expended and at least two potential suppliers were located, negotiations to obtain the crystals in a reasonable time at reasonable cost were unsuccessful. Therefore, we expanded our objective to include the growth of the mixed crystals as well.

II. DESIGN OF HOT-WALL DEPOSITION APPARATUS

One of the problems peculiar to the study of single-crystal copper sulfide - (cadmium, zinc) sulfide heterojunctions is that thin sections of the II-VI crystal are quite fragile and bulk specimens are difficult and time-consuming to dope to sufficiently high conductivity for device studies. In order to obtain thin sections in a manageable form, we decided to adopt a "hot-wall" deposition technique reported in the literature⁽³⁾ to give good single-crystal thin films of ZnS on GaAs substrates. The design of Behrndt and Moreno was modified to include two sources, one each for ZnS and CdS. Also, baffles were installed between the two sources and between the sources and substrate holder. A longitudinal section of the cylindrical apparatus is shown in Fig. 1.

In operation the vacuum system containing the hot-wall apparatus is pumped down into the 10^{-6} Torr range and the cylinder and substrate holder are separately heated to 500-600°C. Then the substrate holder is positioned tightly over the cylinder and allowed to become about

100C° cooler than the cylinder. Then the sources are turned on and the charges evaporate and condense mostly on the cooler surface of the substrates and substrate holder. The substrate temperature is such that the condensing species have quite high surface mobilities so there is a great tendency for the film to be oriented by the substrate.

III. DESIGN FOR SPECTRAL RESPONSE APPARATUS

Fig. 2 shows a schematic outline of the spectral response apparatus as it is currently configured. It was designed and built at this laboratory. The electronic design was done principally by Mr. Paul Salz of our Electronics Research and Development Department.

The output of the tungsten-halide lamp (useable at wavelengths down to about 350nm) is focused through a chopping wheel on the entrance slit of the double grating monochromator. The double grating configuration is used to achieve very low stray light to insure that the "spectral response" measured in the absence of a "secondary" light is truly the monochromatic response. This precaution is deemed necessary since it is known there are sometimes non-linear effects in the kind of cells under study in the case of non-monochromatic illumination. The monochromator is driven by a motor which is interlocked to provide for starting and stopping a scan at predetermined wavelength and to protect the monochromator from being driven past its endpoints. The motor also drives a variable resistor connected to a transresistance amplifier to provide a voltage precisely proportional to the wavelength setting of the monochromator.

The beam emerging from the exit slit of the monochromator is incident on both the cell under test and a thermopile (Sensors, inc. Model L22-18)

whose sensitivity is wavelength independent (within a few percent, in the region from 450 to 9000nm, limited by its window material which is CaF_2). The output of the test cell is amplified by an operational amplifier circuit of very low input impedance ($\lesssim 1\Omega$) to approximate short-circuit conditions; and then synchronously detected and low-pass filtered. The thermopile output is amplified and also synchronously detected and filtered. Then the voltage proportional to the test cell current is divided by the voltage proportional to the thermopile output by two high-precision analog divide circuit modules: one providing an output equal to the ratio in volts; and the other, the logarithm of the ratio with 1 volt equal to 1 decade. One of these two outputs is fed, together with the wavelength-proportional voltage, to an x-y plotting device to give a direct spectral response plot. The linear output is also connected to a digital volt meter whose output is recorded on paper tape at equal wavelength intervals by means of a pulse-train derived from the wavelength voltage. This paper tape record is interpreted and prepared for use in model-fitting studies by the FORTRAN program CONVERT (See Appendix A and Section VI).

IV. FILM GROWTH RESULTS

It was determined there was negligible cross-heating of the evaporation sources in the hot-wall apparatus. Therefore, we hoped it would be possible to determine the growth rates of CdS and ZnS separately and use the results as a first approximation to the correct evaporation conditions for a given Cd-Zn ratio in a co-deposition. A very simple model was found to give a very good fit to the growth rate of CdS deposits under several different growth conditions. However, it was then discovered that, although there was no thermal interaction of the sources, enough

Zn vapor found its way around the baffles to the CdS source to drastically affect the CdS vaporization rate. This result has forced us to an iterative procedure wherein a given combination of source currents is tried and the resulting film composition is determined from the x-ray diffractometer lines (See Appendix B). Then the current settings are changed in the appropriate directions for the next deposition to get closer to the desired composition.

In addition to the x-ray diffractometer measurement which gives a fairly precise determination of the surface layer composition and an idea as to the degree of polycrystallinity, we have measured the film composition as a function of depth by two other means. The more precise of these is the electron microprobe which is used to scan an angle-lapped section of the film. Figure 3 shows the results of such a scan on an early film having large composition gradients. When reasonable care is taken, this kind of measurement gives relative accuracies of the order of 1%.

A more qualitative, but also much more readily performed, measure of the transverse film composition is provided by the energy dispersive x-ray analyzer (EDAX) in the scanning electron microscope (S.E.M.) with the vertical deflection of the beam-scan turned off. Using this technique, one can observe the composition profile at the cleaved edge of the film. Figure 4 is an example of such an experiment performed on the same sample as shown in Fig. 3. Seen in Fig. 4 is a triple exposure of the same area of the specimen, at the same magnification, but in two operating modes. The two white lines graphically depict the film composition vs. depth, i.e., the vertical displacement is proportional to the weight

percent of the element being analyzed. The background "picture" is a normal S.E.M. micrograph taken after the line scans so one can see a darkened band where the electron beam was repeatedly swept for the composition analysis. Note that the electron microprobe and S.E.M. show excellent qualitative agreement.

Figs. 5 and 6 show respectively an EDAX profile of the cleaved edge and a low-magnification S.E.M. micrograph of the top surface of a more recent film. It can be seen that this film is much more nearly uniform than that of Figs. 3 and 4. The x-ray diffractometer scan of the sample of Figs. 5 and 6 showed evidence of some polycrystallinity in the film; and it is thought that the irregular shapes visible primarily on the tips of the hexagonal pyramids of Fig. 6 are responsible for the extra x-ray peaks. The morphology of the cleaved surface suggests that the misoriented grains exist only at the top surface of this sample.

Table 1 summarizes the experimental conditions and results for the most recent group of films. The large scatter in the thicknesses of films grown under apparently similar conditions is thought to be due to escape of the charge at the seam between the hot-wall cylinder and the bottom end-plate. This view is supported by the observation that the background pressure outside the cylinder on some runs is much higher than others where the resulting films are thicker. A new cylinder with an integral baffle and end-plate has been fabricated and will soon be installed, hopefully, reducing this problem.

One interesting result of this study concerns the differences in film growth on the Ga and As faces of the GaAs substrates. The GaAs wafers were supplied with one face polished, and this side was used for runs 1

through 8. However, when it was discovered that the wafers all had been polished on the same crystallographic face, the As (111) or B-face; deposition on the opposite face, the Ga or A-face, was tried. It was found that growth on the Ga face has a greater tendency toward monocrystallinity and, further, it seems to proceed at a higher rate; although, because of the difficulties mentioned earlier, this latter result is less certain. It is thought that this marked difference in growth is possibly due to a difference in stacking sequence in films grown on A- or B-faces.

V. Heterojunction Measurements

The new spectral response measurement apparatus has been used to remeasure the characteristics of the cells reported in Ref. 2 wherein the spectral response had been determined with a single grating monochromator using a d.c. technique and a separate light intensity calibration run. Fig. 7 shows the result of the remeasurement. Comparison of Fig. 7 with the previously measured spectral response curves shows that the light intensity calibration was probably in error in the extreme short wavelength region ($\lambda \lesssim 500$). However, the two techniques agree quite well otherwise; and the new apparatus enables us to extend the measurements reliably to at least an order of magnitude smaller currents.

Only very preliminary results are available for junctions made on the heteroepitaxial films, since only recently have films suitable for device preparation become available. Figure 8 shows the long wavelength part of the spectral response of a $\text{Cu}_x\text{S}-\text{CdS}$ cell formed by the aqueous dipping method on a thin film sample. The contacts to the n- and p-type sides were fired-on indium and conducting silver paint respectively. The

peak observed at about 870nm is thought to be due to a silver paint-CdS barrier, since a similar peak was obtained on a sample prepared in the same manner, but without the Cu_xS -forming dip.

The current-voltage (I-V) characteristics of this cell were also investigated using the apparatus shown schematically in Fig. 9. The I-V measurement results are shown in Fig. 10. Figure 10a shows the characteristic with tungsten lamp illumination; and 10b shows that with natural sunlight (1:30 p.m. P.D.T. October 13, 1976). Notice that the horizontal and vertical scales in these two oscillographs are not the same; and that the open-circuit voltage and short-circuit current for the sunlit case are respectively 5 and 8 times smaller than those obtained in the tungsten lamp illumination. Obviously, the lamp intensity is higher than AMI; but previous cells measured under similar conditions showed such smaller differences between sunlight and tungsten lamp-light. We have no explanation for this observation at this time.

VI. MATHEMATICAL MODELING OF HETEROJUNCTION ELECTRICAL CHARACTERISTICS

The ultimate goal of this research program is a better understanding of heterojunctions like the Cu_xS -(Cd,Zn)S junction. Therefore, an important part of this project is the creation of physical models whose prediction of device characteristics may be compared with experiment. Provided these models are based on physical pictures with no arbitrary functionality, this process will yield further insight as to the mechanisms involved in the photovoltaic effect in this kind of heterojunction.

A modest first step in this direction is the demonstration that the spectral response characteristics of these devices can be accounted for by bulk absorption in the Cu_xS layer with diffusion-controlled transport to

the interface. The method used is to try to fit the experimental data to a model of the junction incorporating the solution of the one-dimensional diffusion equation and a sum of exponential absorption edges known to give a good representation of the optical absorption of $\text{Cu}_x\text{S}^{(4)}$. The fitting is done in the usual, least-squares, sense and is accomplished by the CERN subroutine package MINUIT which uses a variable-metric convergence method for general function minimization. This approach has resulted in reasonably good fits to the preliminary data available, although the absorption parameter values seem to differ somewhat from those of Ref. 4.

The use of an exponential absorption edge is not satisfying in that its physical basis is not readily apparent, so that it seems more-or-less arbitrary. An alternative model, having a clearer physical meaning will be sought.

Appendix A - Conversion of Paper Tape Experimental Record to Input

Data for Model-Fitting Program

The "FORTRAN" program and subroutines on the following pages were written for use on the BKY (LBL) CDC 6600 or 6200 computers as an "interactive" job; i.e., the program flow is controlled from a remote terminal, so that decisions regarding the data processing can be made during program execution. In operation one reads the paper tape of an experiment via a Teletype ^(R) paper tape reader onto a disk file and then begins execution of CONVERT. CONVERT asks for the name of the disk file, reads it, computes an n-th order difference table (n supplied by the operator) and asks the operator if the apparent noise-level (computed from the n-th differences⁽⁵⁾) is reasonable. If the noise-level is too high, (indicating a probable mis-punch on the tape) a scan is made through the n-th differences to find the probable error(s). Also, provision is made for smoothing the data by digital filtering⁽⁶⁾. Since the paper tape does not include the wavelength value at each point, these are also computed from the endpoint values for later convenience. Finally, provision has been made to have CONVERT prepare and append to its output file (specified by the operator) a set of "parameter" and "command" cards in a format recognizable by the CERN subroutine package MINUIT used for model fitting (See Sec. VI).

PROGRAM CONVERT (INPLT=50,OUTPUT=50,PUNCH)

```

1.      PROGRAM CONVERT (INPUT=50,OUTPUT=50,PUNCH)
C
C      THIS PROGRAM READS A LOCAL FILE PREVIOUSLY CREATED FROM A PAPER
C      TAPE CONSISTING OF A SERIES OF TERMS OF THE FORM <SAAAAB,LF,CR>
C      WHERE S = < ,-> AND AAAAB REPRESENTS .0AAAA*10**B.
C
C      IT WILL ALSO (OPTIONALLY) PREPARE A SEQUENCE OF PARAMETER AND
C      COMMAND CARDS SUITABLE AS INPUT TO THE CEPN SUBROUTINE PACKAGE
C      <MINUIT> AVAILABLE AT BKY. THE PROGRAM CONTAINS SEVERAL NON-ANSI
C      FEATURES PECULIAR TO THE MAF COMPILER AND THE BKY OPERATING SYSTEM
C      AND IS THEREFORE NOT VERY PORTABLE.
C
C
C              TERRY M. PETERSON (X5515)
C
2.      COMMON KARD(8), SCC(1200), ALAM(1200)
3.      EQUIVALENCE (CIF,ALAM)
4.      COMMON /FIND/ ICARD (8), IFMT(3), LAST(5)
5.      DIMENSION CIF(1200), COEF(11)
6.      LOGICAL INVALID, CDC
7.      DATA IOUT /6LOUTPUT/, IIN, IPUNCH /5LINPLT,5LPUNCH/
8.      DATA CCEF /1.0,-4.0,6.0,-4.0,1.0,6*0.0/, NDFP1 /5/
9.      DATA NDIF /4/, UNDEF /1LE/, FACTOR /0.1195/
10.     DATA IBLNK /10H /
C
C              READ AND WRITE AT TERMINAL
11.     CALL FETSET(6LOUTPUT,7LTAPETTY,4)
12.     CALL FETSET(5LINPLT,7LTAPETTY,8)
13.     PRINT*, * BEGIN CONVERT*,/,* ENTER TITLE CARD*
14.     ENDFILE ICUT
15.     READ(100, KARD)
16. 100   FORMAT (8A10)
17.     PRINT*, * NOW ENTER WAVELENGTH ENDPOINTS (LOWER FIRST)*
18.     ENDFILE IOUT
19.     NREAD = 1
20. 2001  READ(.FPR.=2000,IIN,) ALAM1, ALAM2
21.     PRINT*, * NOW ENTER DIF. ORDER NO. FOR ERROR-CHECK*
22.     NREAD = 2
23.     ENDFILE ICLT
24. 2002  READ(.FPR.=2000,IIN,) NTEM
25.     IF (NTEM) 7,7,6
26. 6     IF (NTEM - 10) 4,4,3
27. 3     PRINT *, * NO. TOO LARGE - PLEASE RE-ENTER*
28.     ENDFILE ICLT
29.     GO TO 2002
30. 4     NCIF = NTEM
31.     FACTOR = 1.0
32.     DO 1 I=1,NDIF
33.     FACTOR = FACTOR*FLCAT(I)
34. 1     CONTINUE
35.     J1 = NDIF+1 4 J2 = 2*NDIF
37.     FACTOR2 = FACTOR
38.     DO 2 I = J1,J2
39.     FACTOR2 = FACTOR2*FLOAT(I)
40. 2     CONTINUE
41.     FACTOR = FACTOR/SQRT(FACTOR2)
42.     CDC = .F.
43.     IF (2*(NDIF/2) .NE. NDIF) CDC = .T.
44.     IF (CDC) GO TO 8
45.     NDFP1 = NDIF + 1

```

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**PROGRAM CONVERT (INPLT=50,CUTFLT=50,PLNCH)**

46.      DO 5 J=1,NDIF
47. 5      CCEF(J+1) = CCEF(J)*FLCAT(J-NDIF1)/FLCAT(J)
48.      GO TO 8
49. 7      PRINT *, * C.C.NC. .LE. 0.0 -      4 ASSUMED.*
50. 8      PRINT *, * WHAT FILE IS THE S.C.C. DATA CN?*
51.      ENDFILE IOUT
52. 9      LNAME = IPUNCH
      C
      SET UP FILE NAME FOR NEXT READ
53.      CALL FILCHG (LNAME)
54.      DO 10 I = 1,1200
55.      READ(.FND.=11,.ERR.=3000,IPUNCH,125) ISCC, N
56. 3001    SCC(I) = FLOAT(ISCC)*10.C**(N-5)
57. 125    FORMAT(I5,11)
58. 10      CONTINUE
59.      I = 1200
60. 11      I = I - 1
61.      IF (I) 1000,1000,12
62. 12      PRINT*, I, * DATA PTS. WERE READ*
      C
      COMPUTE NOISE-LEVEL ESTIMATE
63.      ENDFILE IOUT
64. 105     DO 119 J = 1,I
65.      DIF(J) = SCC(J)
66. 119     CONTINUE
67.      DO 121 J=1,NDIF
68.      K2 = I - J
69.      DO 120 K = 1,K2
70.      DIF(K) = CIF(K+1) - CIF(K)
71. 120     CONTINUE
72. 121     CONTINUE
73.      SUM = C.C
74.      DO 122 K=1,K2
75.      SUM = SUM + CIF(K)**2
76. 122     CONTINUE
77.      DBAR = SQRT(SUM/FLCAT(K2))
78.      NBIG = 0
79.      DO 1221 K=1,K2
80.      IF (ABS(DIF(K)) .GT. DBAR) NBIG = NBIG + 1
81. 1221     CONTINUE
82.      PRXERR = DBAR*FACTOR
82.      PRINT 175, NDIF, PRXERR
84. 175     FORMAT (* THE NOISE-LEVEL, EST. FROM THE *I4*TH. DIF., IS *G10.2)
85.      PRINT 700, NBIG
86. 700     FORMAT (* THERE ARE *I3* POINTS WITH <LARGE> DIFFERENCES.*)
87.      IF (NBIG*7 .LT. K2) GO TO 1223
88.      PRINT *, * AN ERROR SCAN WILL PROBABLY NOT BE USEFUL.*,/,
      1      * DO YOU WISH TO FILTER THE DATA INSTEAD?*
89.      ENDFILE IOUT
90.      IF (ACYES(MAYBE)) 1223,1223,1222
91. 1222     CALL SMOOTH (I,ALAM1,ALAM2)
92.      GO TO 131
93. 1223     PRINT *, * SHOULD AN ERROR-SCAN BE DONE?*
94.      ENDFILE IOUT
95.      IF (ACYES(MAYBE)) 131,131,1226
96. 1226     KLOSE = MAXC(1,NDIF/2)
97.      DO 123 K = 1,K2,KLOSE
98.      IF (ABS(CIF(K)) .LT. DBAR) GO TO 123
99.      K1 = MINC(I,K+NDIF)
100.      PRINT 195, K, K1, NDIF
101.      ENDFILE IOUT

```



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**PROGRAM CONVERT (INPUT=50,OUTPUT=50,PLNCH)**

102. 195  FORMAT (* POSSIBLE ERROR BETWEEN DATA POINTS *I4* AND*I4*,*/
1      1 * VALUES AND *I2*TH DIFFERENCES FOLLOW. . .*)
103.      DO 1965 KK=K,K1
104.      SC = SCC(KK)
105.      CIF1 = UNDEF
106.      KC = KK - KLCSE
107.      IF (KD .GT. 0 .A. KC .LE. K2) DIF1 = DIF(KC)
108.      IF (KC .NE. K .O. ODD) GO TO 1955
109.      SUM = PRXERR = 0.0
110.      KDIF = KD - (KLCSE + 1)
111.      DO 1953 L = 1,NDFP1
112.      KDIF = KDIF + 1
113.      IF (KDIF .LE. 0 .C. KDIF .GT. K2) GO TO 1953
114.      PRXERR = PRXERR + SIGN(1.0,COEF(L))*DIF(KDIF)
115.      SUM = SUM + ABS(COEF(L))
116. 1953  CONTINUE
117.      PRXERR = SC - PRXERR/SUM
118.      PRINT 1954, KK,SC,CIF1,PRXERR
119. 1954  FORMAT (I10,2G12.4* SUGGESTED VALUE =G12.4)
120.      GO TO 1965
121. 1955  PRINT 196, KK, SC, CIF1
122. 196   FORMAT (I10,2G12.4)
123. 1965  CONTINUE
124. 127   CONTINUE
125.      PRINT *, * DO YOU WISH TO ALTER ANY OF THE QUESTIONABLE DATA?
126.      ENDFILE ICUT
127.      IF (NOYES(MAYBE)) 131,131,127
128. 127    PRINT *, * OK - ENTER THE INDEX AND NEW VALUE FOR EACH POINT *
1      1 ,*TC BE CORRECTED.*,/,* TC STOP, ENTER 0,0*
129.      NREAD = 2
130.      ENDFILE IOUT
131. 128    READ (.ERR.=2000,IIN,) K, SCCCCR
132.      IF (K) 130,130,129
133. 129    SCC(K) = SCCCCR
134.      GO TO 128
135. 130    PRINT *, *RECALC. NOISE LEVEL?
136.      ENDFILE ICUT
137.      IF (NOYES(MAYBE)) 131,131,105
138. 131    DELLAM = (ALAM2-ALAM1)/FLOAT(I-1)
139.      PRINT *, * WHAT FILE IS DATA TO BE WRITTEN ON?
140.      ENDFILE IOLT
141.      LNAME = IPUNCH
142.      CALL FILCHG (LNAME)
143.      PUNCH 100, KARD
144.      PUNCH 150, I
145. 150    FORMAT(I10)
146.      DO13 J = 1,I
147.      ALAM(J) = ALAM1 + DELLAM*FLOAT(J-1)
148. 13     CONTINUE
149.      PUNCH 200, (ALAM(J), SCC(J), J=1,I)
150. 200    FORMAT (7(F6.1,F5.4))
151.      IR = MCD(I,7)
152.      I = 2 + I/7
153.      IF (IR .GT. 0) I = I + 1
154.      II = 0
155.      PRINT*, * THE DATA ARE(2) WRITTEN.*,/,
1      1 * ARE THERE MINUIT CARDS?
156.      ENDFILE IOLT
157.      IF (NOYES(MAYBE)) 19,19,14

```

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**PROGRAM CONVERT (INPLT=50,OUTPUT=50,PUNCH)**

C                                     PREPARE MINUIT CARD SEQ.
158. 14   PRINT*, * HOW MANY PARAMS.?*
159.      ENDFILE ICUT
160.      NREAD = 4
161. 2004 READ (.ERR.=2000,IIN,) NPAR
162.      PUNCH 100, KARD
163.      PRINT*, * FOR EACH PARAM., ENTER*,/,* 1) NAME (IN QUOTES)*
1        ,/,* 2) INITIAL VALUE*,/,* 3) INITIAL STEP SIZE*,/,
2        * 4 AND 5) LOWER AND UPPER BOUNDS*
164.      NREAD = 5
165.      DO15 J = 1,NPAR
166.      PRINT *, * ENTER PARAM.*,J
167.      ENDFILE ICUT
168. 2005 READ (.ERR.=2000,IIN,) NAM, VAL, STEP, EL, EU
169.      PUNCH 300, J, NAM, VAL, STEP, BL, BL
170. 300   FORMAT(I10,A10,4C10.4)
171. 15    CONTINUE
172.      PUNCH100, IBLNK
173.      II = NPAR + 2
174.      PRINT*, * NOW ENTER MINUIT COMMANDS*
1        ,/,* PROCESSING STOPS UPON ENCOUNTERING AN*,/,
2        * END, EXIT, OR END RETURN COMMAND.*
175.      ENDFILE ICUT
176. 16    READ100, KARC
177.      IF (INVALID(KARC)) GO TO 16
178.      II = II + 1
179.      PUNCH 100, KARC
180.      IF (KARC-4HEXIT)17,19,17
181. 17     IF (KARC-3HEND)18,19,18
182. 18     IF (KARC-10HEND RETURN)16,19,16
183. 19     PRINT 400, I, II, LNAME
184.      ENDFILE ICUT
185. 400   FORMAT(* CONVERT SUCCESSFUL - - */IS* DATA **I3* MINUIT*
1        * CARDS WRITTEN TO FILE *A7)
186.      STOP
C                                     BAD INPUT FILE NAME
187. 1000  PRINT 1010, LNAME
188. 1010  FORMAT(* IS FILE NAME <*A7*> CORRECT?*)
189.      ENDFILE ICUT
190.      IF (NOYES(MAYBE)) 1030,1030,86
191. 1030  PRINT *, * OK - RETRY*,/,* ENTER FILE NAME*
192.      ENDFILE ICUT
193.      GO TO 9
194. 2000  PRINT *, *E E E INCORRECT DATA FORM*,/,
1        * PLEASE RE-ENTER ITEM(S) OF LAST REQUEST.*
195.      ENDFILE ICUT
196.      GO TO (2001,2002,128,2004,2005,2006), NREAD
197. 3000  PRINT *, *E E E READ DATA PT. - MUST CORRECT BEFORE PROCEEDING.*,
1        ,/,* I = *,I
198.      REWIND IPUNCH
199.      IF (I .LT. 10) GO TO 3020
200.      ENCCDE (30,3010,IFMT) I - 6
201. 3010  FORMAT(*(*I11*(/),5(A10,/),8A10)*)
202.      READ (IPUNCH,IFMT) LAST, ICARD
203.      PRINT *, * INPLT RECCRD = *,/,ICARD,/,*++++*
204.      PRINT 3011
205. 3011  FORMAT(* ONLY INTEGERS ALLOWED IN FIRST 6 COLS.*)
206.      PRINT *, * LAST FIVE PTS. WERE*
207.      GO 3012 J = 1,5

```

```

208. PRINT *, LAST(J)
209. 3012 CONTINUE
210. GO TO 3040
211. 3020 PRINT *, # LINES READ =#
212. DO 3025 J=1,I
213. READ (IPLNCH,3021) ICARD
214. PRINT 3021, ICARD
215. 3021 FORMAT(8A10)
216. 3025 CONTINUE
217. PRINT 3011
218. 3040 PRINT *, # ENTER CORRECTION#
219. NREAD = 6
220. ENDFILE ICUT
221. 2006 READ (,ERR.=2000,IIN,) ISCCCR
222. ISCC = ISCCCR/10
223. N = ISCCCR - ISCC*10
224. PRINT *, # OK - READING CF <#,LNAME,#> RESUMED.#
225. GO TO 3001
226. E6 PRINT, #E E E E E R R C R - NO DATA FOUND ON SPECIFIED FILE#
227. ENDFILE ICUT
228. STOP 1
229. END

```

1. SUBROUTINE SMOOTH (APP,AL1,AL2)

```

C      PERFORMS SMOOTHING OF UNIFORMLY SPACED DATA (IN SCC) AND
C      READJUSTS END PTS. OF INDEPENDENT VARIABLE (AL1,AL2)
C      TO ACCOUNT FOR PTS. LOST IN SMOOTHING.
C
2.      DIMENSION COEF(6)
3.      COMMON KARD(8), SCC(1200), ALAM(1200)
4.      DATA COEF /1.,2.,3.,3.,2.,1./
5.      NP = NPP
6.      DL0 = (AL2-AL1)/FLOAT(NP-1)
7.      DL = 2.5*DL0
8.      AL1 = AL1 + DL
9.      AL2 = AL2 - DL
10.     NP2 = NP/2
11.     IF (2*NP2 .NE. NP) AL2 = AL2 - DL0
12.     NF = NP2 - 2
13.     KC = -2
14.     DO 10 I= 1,NP
15.     KO = KO + 2
16.     S = 0.0
17.     DO 5 K = 1,6
18.     S = S + COEF(K)*SCC(K+KO)
19.     SCC(I) = S/12.0
20. 10  CONTINUE
21.     NPP = NP
22.     RETURN
23.     END

```

SUBROUTINE FILCHG(LNAME)

```

1.      SUBROUTINE FILCHG(LNAME)
      C
      C      READS <NAME> AND CHANGES NAME OF <LNAME> TO <NAME>.
      C
2.      DATA LCHAR /7700 0000 0000 0000 0000/
3.      NCHAR = 0
4.      READ 1, NAME
5. 1    FORMAT(A10)
6.      DO 5 I = 1,10
7.      IF ((NAME .A. 77B) .NE. 55B) NCHAR = NCHAR + 1
8.      NAME = SHIFT(NAME,6)
9. 5    CONTINUE
10.     ITEM = NAME
11.     DO 6 I = 1,9
12.     ITEM = SHIFT(ITEM,6)
12.     IF ((ITEM.A.77B) .NE. 55B) GO TO 7
14.     NAME = ITEM
15. 6    CONTINUE
16. 7    MSK = SHIFT(LCHAR, -(6*(NCHAR-1)))
17.     NAME = NAME .A. MSK
18.     CALL FETSET(LNAME,NAME,1)
19.     REWIND LNAME
20.     LNAME = NAME
21.     RETURN
22.     END

```

SUBROUTINE FETSET (LNAME,NNAME,IC)

```

1.      SUBROUTINE FETSET (LNAME,NNAME,IC)
      C
      C      CHANGES NAME OF FILE <LNAME> TO <NNAME>. ALSO SETS FET BITS
      C      ACCORDING TO VALUE OF <IC> AS FOLLOWS...
      C          ABS(IC) .GE. 2 = SET AUTO-RECALL
      C          ABS(IC) .GE. 6 = SET AUTO-RECALL AND WAIT-FCR-REAL-DATA.
      C
2.      DIMENSION IFET (8)
3.      DATA MASK1/0000 0030 0000 0000 0000B/
4.      DATA MASK2/4000 0000 0000 0000 0000B/
5.      NWD = IABS(IC)
6.      CALL FET(LNAME,IFET,8)
7.      IFET(1) = NNAME .C. 1B
8.      IF (NWD .LT. 2) GO TO 10
9.      IFET(8) = IFET(8) .O. MASK2
10.     IF (NWD .LT. 6) GO TO 10
11.     IFET(2) = IFET(2) .C. MASK1
12. 10    CALL FET(LNAME,IFET,-8)
13.     RETURN
14.     END

```

FUNCTION NOYES (MAYBE)

```

1.      FUNCTION NOYES (MAYBE)
      C
      C   READS AND RECOGNIZES YES/NO ANS. IN AT LEAST 7 LANGUAGES.
      C   RETURNS -1 FOR <NO>, +1 FOR <YES>, AND REFUSES TO ACCEPT
      C   UNRECOGNIZED RESPONSE.
      C
2.      INTEGER YES (5)
3.      DATA YES /2LAF,2LSI,2LOU,2LJA,2LDA/, IOUT /6LOUTPLT/
4. 10    READ 1, MAYBE
5. 1      FORMAT(A10)
6.      DO 2 I = 1,10
7.        LET = MAYBE .A. 11;
8.        IF (LET .NE. 1L ) GO TO 4
9.        MAYBE = SHIFT(MAYBE,6)
10. 2      CONTINUE
11. 3      PRINT *, * QUESTION REQUIRES YES/NO ANS.*
12.      ENDFILE IOUT
13.      GO TO 10
14. 4      IF (LET .NE. 1LN) GO TO 5
15.      NOYES = -1
16.      RETURN
17. 5      IF (LET .EQ. 1LV) GO TO 7
18.      MAYBE = MAYBE .A. 2L;;
19.      DO 6 I = 1,5
20.        IF (MAYBE - YES(I)) 6,7,6
21. 6      CONTINUE
22.      GO TO 3
23. 7      NOYES = 1
24.      RETURN
25.      END

```

LOGICAL FUNCTION INVALID(K)

```

1.      LOGICAL FUNCTION INVALID(K)
      C
      C   RETURNS .FALSE. FOR VALID MINUIT COMMAND <K>.
      C
2.      DIMENSION MINCOM(22)
3.      DATA NMC /22/
4.      DATA MINCOM /10+MINIMIZE ,10HSIMPLEX ,10HMIGRAD ,
1 10HRESTORE ,10HGRACIENT ,10HEXIT ,10HEND ,
2 10HERROR DEF ,10HHESSE ,10HEND RETURN,10HCALL FCA ,
3 10HIMPRVE ,10HFLNCH ,10HCCVARIANCE,10HCONTOUR ,
4 10HSEFK ,10HPRINTOLT ,10HPAGE ,10HATCUT ,
5 10HSTANDARD ,10HMINOS ,10HFIX /
5.      DATA ICLT /6LOUTPLT/
6.      INVALID = .T.
7.      DO 1 I=1,NMC
8.        IF(K - MINCOM(I)) 1,2,1
9. 1      CONTINUE
10.     PRINT*, * UNRECOGNIZED COMMAND, PLEASE RETRY*
11.     ENDFILE ICLT
12.     RETURN
13. 2      INVALID = .F.
14.     RETURN
15.     END

```

Appendix B - An SR-52 Utility Program for Use with the X-Ray Diffractometer
in (Cd,Zn)S Studies

Since it is often handy to know, during a diffractometer scan, the "d-spacing" corresponding to a given "2 θ " peak; and since the d-spacings in (Cd,Zn)S can be used to determine the composition⁽⁷⁾, the following program was written for a Texas Instruments SR-52 calculator to perform conversions of "2 θ " to "d-spacing" and d(hkl) to ZnS fraction (for both hexagonal and cubic indicies) and their inverses.

The "2 θ " $\leftrightarrow$ "d-spacing" conversion is a straightforward calculation using the Bragg formula,

$$\lambda = 2d \sin \theta$$

where λ is the x-ray wavelength.

The conversion from d(hkl) to ZnS fraction is made by assuming the d-spacing to be linear in the ZnS fraction (a reasonable assumption, see Ref. 7) and using the formula

$$X_{\text{ZnS}} = \frac{d(\text{hkl}) - d_{\text{ZnS}}(\text{hkl})}{d_{\text{CdS}}(\text{hkl}) - d_{\text{ZnS}}(\text{hkl})} \equiv \frac{d(X) - d(1)}{d(0) - d(1)}$$

where $d_{\text{ZnS,CdS}}(\text{hkl})$ are calculated from

$$d_i(\text{hkl}) = \begin{cases} \frac{a_i}{[h^2 + k^2 + l^2]^{\frac{1}{2}}} & \text{for cubic indicies} \\ \frac{a_i}{\left[h^2 + k^2 + hk + \frac{3a_i^2 l^2}{4c_i^2} \right]^{\frac{1}{2}}} & \text{for hexagonal indicies} \end{cases}$$

where a_i , c_i are the lattice constants, taken from Ref. 7. The conversion from X_{ZnS} to $d(hkl)$ can obviously be made using the same equations. The accuracy of this procedure has been checked using the data of Ref. 7; and has been found to be within about 1%, relative.

The user instructions are as follows:

- I. Load program into memory and set calculator in degree-angle mode.
- II. To convert:
 - A. $2\theta \rightarrow d\text{-spacing}$
 - 1) Enter 2θ .
 - 2) Press key D. Display will show d-spacing
 - B. $d\text{-spacing} \rightarrow 2\theta$
 - 1) Enter d-spacing
 - 2) Press key D'. Display will show 2θ .
 - C. $d(hkl)_{\text{hex(cubic)}} \rightarrow X_{\text{ZnS}}$
 - 1) Enter d-spacing
 - 2) Press key A(B)
 - 3) When display shows "3." enter "hk.l"("hkl").
 - 4) Press key RUN. Display will show X_{ZnS}
 - D. $X_{\text{ZnS}} \rightarrow d(hkl)_{\text{hex(cubic)}}$
 - 1) Enter X_{ZnS}
 - 2) Press key A'(B')
 - 3) When display shows "3." enter "hk.l"("hkl").
 - 4) Press key RUN. Display will show $d(hkl)_{\text{hex(cubic)}}$.

DIFFRACTOMETER UTILITY PROGRAM LISTING

LOC.	MNEMONICS	COMMENTS
000	HLT	
001	LBL E' (RCL × RCL 98-10)	Calc. $\left(1 - \frac{\Delta a}{a}\right)^2 \times 100$
013	$\times^2$ rtn	
015	LBL E STO 98	Calc. d(X). assumes
020	(RCL 15 ÷ .77 E'	R ₁₄ and R ₁₅ contain
029	+RCL 14 ÷ .696 E')	appropriate combinations
040	$\sqrt{x}$ 1/x rtn	of h,k,l; a,c.
043	LBL C CMs fix 0	Get hkl
048	3 STO 00	
052	(HLT if flg 0 fix	Halt for hkl entry
057	÷ 100	Skip this for cubic indicies
061	LBL fix ×10 - STO 01 .49)	
074	EE INV EE x	Decode hkl
078	(IND STO 00 SUM 14	
086	$\sqrt{x}$ +/- + RCL 01)	
093	(RCL dsz fix	
097	fix 2 INV ifflg 0 115	Set up appropriate
105	2.956) PROD 14 rtn	constants for subroutine
115	RCL 01 ×2.217) STO 14	E in R ₁₄ and R ₁₅
128	(RCL 03 STO 15 $\sqrt{x}$ ×	
137	RCL 02 SUM 15 $\sqrt{x}$) SUM 15	
148	7.79 PROD 15 rtn	
156	LBL B stflg 0	Set flag 0 to indicate cubic
160	LBL A (STO 99 - C	indicies.
168	0 E STO 19)	Calc. $X_{ZnS} = \frac{d(X)-d(0)}{d(1)-d(0)}$
175	(1 E - RCL 19 = rset	Go to 000 and reset flag 0
184	LBL B' stflg 0	Set flag 0 for cubic mode
188	LBL A' + C 0 = E rset	Get indicies and calc.
196	LBL D ÷ 2 = sin 1/x	d(X)
203	× .77 = rtn	Calc. $\lambda/2\sin(\theta)$
209	LBL D' 1/x × .77 = INV sin	Calc. 2 arcsin($\lambda/2d$)
219	× 2 = rtn	

Table I

Run	ZnS Current (amps)	CdS Current (amps)	Deposition Time (minutes)	Substrate Temp. (°C)	Cylinder Temp. (°C)	Crystallinity s = single p = poly	Thick- ness (μm)	Composition y in Cd _{1-y} Zn _y S for (hkl)
1	46	30	60	495	600	p	30	(002) y = .15, .86 (103) y = .26 (004) y = .22
2	46	25	60	480	600	p	30	(002) y = .10 (002) ZnS (102) y = .08 (103) y = .10
3	43	25	60	485	600			Non-uniform
4	41	23	60	470	600	p	~24	(002) y = .13 (102) y = .20 (103) y = .15 (104) y = .10
5	37	20	90	460	600	p	7	(002) ZnS (102) y = .31 (103) y = .29
6	37	20	90	420	550	s	~2	(002) ZnS
7	39	23	90	420	550	s	~3	(002) y = .70 Broad x-ray peak
8	39	24	180	430	560	p	~11	(002) y = .8 (102) y = .28 (103) y = .29
9	39	24	110	430	560 As face Ga face Unpol.	p p	10 10-45	(002)CdS (101)y = .10 (102) y = .13 (103)y = .13 (002) y = .10 (102)y = .12 (103) y = .15 (104)y = .15
10 Ga face pol.	39	24	110	430	560	p	12-20	(102) y = .10 (103) y = .11
11 Ga face pol.	37	22	180	420	560	"s"	<1-13	(002) y = .15 (002) y = .75
12 Ga face pol.	37	22	180	395	560		<1	second baffle used
13 Ga face Unpol.	38	22	180	450	600	s	<1	(002) ZnS (004) ZnS

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FIGURE CAPTIONS

- Fig. 1. Longitudinal cross-section of hot-wall deposition apparatus.
- Fig. 2. Block diagram of spectral response apparatus.
- Fig. 3. Plot of ZnS fraction vs. depth in mixed-crystal film as measured by electron microprobe scan of angle-lapped surface.
- Fig. 4. Scanning electron micrograph and EDAX line-scans of cleaved edge of same film as Fig. 3.
- Fig. 5. EDAX line-scan of nearly uniform mixed-crystal film.
- Fig. 6. Scanning electron micrograph of top surface of the same film as Fig. 5.
- Fig. 7. Spectral response of early cells as measured on new apparatus.
- Fig. 8. Spectral response of Cu_xS -CdS junction made on a recent film.
- Fig. 9. Block diagram of current-voltage measurement apparatus.
- Fig. 10(a). Current-voltage relation under tungsten lamp for Cu_xS -CdS junction; (b) as in (a), but under sunlight.

XBL 771-4942

FIG. 1

FIG. 2

FIG. 3

XBB 771-148

FIG. 4

FIG. 5

XBB 771-149

FIG. 6

XBL 763-6642

FIG. 7

XBL 771-4944

FIG. 8

-34-

XBB 771-147

FIG. 10

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