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**CADMIUM SULFIDE - COPPER SULFIDE
HETEROJUNCTION CELL RESEARCH**

Quarterly Report

September 1 - November 30, 1980

XS-9-8309-1

February 1981

**Institute of Energy Conversion
University of Delaware
Newark, Delaware 19711**

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1. ABSTRACT

Cell yield data for both $\text{Cu}_2\text{S}/\text{CdS}$ and $\text{Cu}_2\text{S}/(\text{CdZn})\text{S}$ are reported. The presence of cracking in the n-type films is reported and the influence of composition and substrate material described. Design efforts for an analytical device that is basically a CdS cell on a transparent substrate, and a low cost gridding procedure are reported. A laser scanning system has been developed to detect incipient shorts and shunting in ungridded cells.

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3. INTRODUCTION

During the first year of this contract, development of a $\text{Cu}_2\text{S}/(\text{CdZn})\text{S}$ solar cell resulted in an energy conversion efficiency of just over 10%(1). The improved understanding and control of the deposition of the $(\text{CdZn})\text{S}$ film that developed during the year provides a good foundation for further advances in efficiency. This is planned to be the result of increasing the zinc content to yield higher cell voltages. Also, during the year it became quite evident that, although higher short circuit currents could be anticipated for a Cu_2S based cell, the present knowledge and technology are incapable of achieving further advances.

The program established for the six months from September 1980 to March 1981 is focused on the practical realization of higher efficiencies in $\text{Cu}_2\text{S}/(\text{CdZn})\text{S}$ cells and improving the knowledge base of the critical Cu_2S layer. Although a fair degree of control of the CdS/ZnS concentric source has been achieved, the source suffers from some significant limitations. Relative rate control is only adjustable by changing the CdS and ZnS orifice sizes and temperature control of a powder compact heated radiatively from the crucible walls is of limited precision. Three independently controlled elemental sources, each vaporizing from the liquid state is being investigated as a preferable alternative to the present system.

In order to develop information on the properties of Cu_2S that is directly relatable to cell performance, a special heterojunction device is being developed. This will be a $\text{Cu}_2\text{S}/\text{CdS}$ junction on a transparent substrate with preferably a transparent contact to the Cu_2S . This structure will allow current-voltage, capacitance, resistance, spectral response, and other measurements to be made on Cu_2S in an active device of known efficiency. The first efforts to deposit CdS on glass slides with either conductive oxide coatings or a metal grid are described.

Other areas under active development are low cost grids which will minimize use of gold, and laser scanning to detect macroscopic defects. Although it would appear that initial cell efficiency is relatively insensitive to local shunts or shorting paths, the long term stability is likely to be very strongly influenced. Laser scanning of ungridded cells is being developed to detect and monitor localized defects.

4. CELL PRODUCTION, TESTING AND ANALYSIS

The major $\text{Cu}_2\text{S}/\text{CdS}$ cell production effort at IEC during this quarter was carried out as part of the Battelle Stability Program, XZ-0-9169. Useful data on reproducibility and the occurrence and elimination of defects in cells were developed and are reported here. Preliminary experiments were carried out on the fabrication of $\text{Cu}_2\text{S}/\text{CdS}$ cells on a transparent substrate and a device configuration for the development of low cost grids was designed. Experiments on $\text{Cu}_2\text{S}/(\text{CdZn})\text{S}$ cells were focused on determining the origins of cracks in the $(\text{CdZn})\text{S}$ films and eliminating the cracks by suitable changes in materials and production techniques.

4.1 Cu₂S/CdS CELL PRODUCTION

Cell Yield

223 Cu₂S/CdS cells were made during this period. Figure 1 shows a histogram of the Cu₂S/CdS cells processed. Table 1 lists the I-V parameters of these cells in order of efficiency. There were clearly difficulties in yield and performance. During the latter part of November, the origin of some of the difficulties was identified as being the surface state of the copper substrate. The electrocleaning process was not removing all blemishes, of which the number and severity seemed to be increasing towards the end of the roll of copper. New materials was ordered, and this coupled with improved attention to general handling and cleaning procedures, seemed to generally eliminate the problem.

Figure 2a shows the desired surface finish after electrocleaning the raw copper-foil. Defects, visible as dark spots still present after electrocleaning, are revealed as a distribution of fine particles by SEM. (Figure 2b.) This is almost certainly an oxide or other corrosion product that is resisting the electrocleaning process.

During this quarter, 42 new CdS substrate were evaluated from the cells they produced. Table 2 shows the best efficiency cell resulting from each substrate. Using 8% as the cut-off criteria for CdS, only 3 substrates qualified during this quarter. This low rate of qualification is directly attributable to the difficulties described above.

MIDDLE OF INTERVAL	NUMBER OF OBSERVATIONS	# OF CELLS
EFF. 0.0	33	*****
0.5	5	*****
1.0	0	
1.5	4	****
2.0	5	*****
2.5	2	**
3.0	1	*
3.5	3	***
4.0	1	*
4.5	9	*****
5.0	12	*****
5.5	10	*****
6.0	22	*****
6.5	38	*****
7.0	24	*****
7.5	20	*****
8.0	9	*****
8.5	2	**

FIGURE 1: Histogram of 223 $\text{Cu}_2\text{S}/\text{CdS}$ made during September through
November, 1980.

TABLE 1

Cu₂S/CdS cells made from 9/80 to 11/80 ranked with respect to Eff.

Eff RANK	CELL #	MAX. EFF.	J _L /100mW	V _{oc} at 25mA	FF	R _s	GSH
00001	21195.113	8.41	22.24	.5180	74.2	1.22	1.48
00002	21193.112	8.28	22.16	.5202	73.1	1.48	1.73
00003	21195.111	8.19	21.86	.5171	73.7	1.50	1.24
00004	21301.114	8.09	21.63	.5113	74.4	1.24	1.18
00005	21301.112	8.00	22.11	.5085	72.5	1.33	2.19
00006	21276.114	7.94	21.63	.5239	71.6	1.65	2.45
00007	21195.123	7.91	21.18	.5171	73.6	1.38	1.55
00008	21179.113	7.86	21.10	.5190	73.3	1.45	1.69
00009	21179.114	7.85	20.72	.5190	74.5	1.10	1.52
00010	21193.111	7.81	21.74	.5173	71.0	1.88	2.33
00011	21193.123	7.75	20.96	.5179	72.6	1.48	1.82
00012	21278.112	7.73	22.21	.5256	68.0	2.22	3.95
00013	21193.114	7.70	21.60	.5261	69.4	2.27	2.84
00014	21193.113	7.67	20.91	.5164	72.6	1.60	1.81
00015	21170.113	7.66	20.67	.5201	72.8	1.74	1.49
00016	21172.123	7.61	20.82	.5202	71.9	1.67	2.19
00017	21170.213	7.59	21.02	.5223	70.8	1.99	2.36
00018	21220.111	7.59	21.38	.5189	70.0	2.20	2.45
00019	21276.113	7.58	20.65	.5227	71.9	1.56	2.41
00020	21278.114	7.56	21.35	.5183	70.1	1.86	3.01
00021	21271.113	7.54	20.10	.5239	73.2	1.72	1.38
00022	21170.111	7.49	20.18	.5235	72.6	1.61	1.90
00023	21263.112	7.46	20.80	.5268	69.8	2.34	2.50
00024	21258.211	7.44	20.54	.5289	70.3	2.13	2.60
00025	21259.121	7.42	20.73	.5319	69.1	2.44	2.89
00026	21260.112	7.41	20.46	.5315	70.0	2.21	2.71
00027	21276.112	7.36	21.13	.5247	68.4	1.87	4.19
00028	21259.123	7.35	20.50	.5317	69.3	2.51	2.68
00029	21263.113	7.34	20.66	.5217	69.9	2.15	2.70
00030	21300.112	7.26	21.10	.5080	69.6	1.83	3.23
00031	21258.213	7.25	19.95	.5289	70.5	2.11	2.48
00032	21267.113	7.21	20.10	.5236	70.4	2.09	2.50
00033	21258.214	7.19	19.61	.5300	71.1	1.92	2.46
00034	21261.114	7.12	19.19	.5259	72.5	1.72	1.87
00035	21259.122	7.11	20.37	.5340	67.5	2.47	3.94
00036	21290.114	7.09	20.99	.5265	66.3	3.13	3.59
00037	21263.114	7.03	20.59	.5290	66.7	2.66	4.11
00038	21277.113	7.01	19.69	.5241	70.0	2.09	2.79
00039	21170.124	6.99	18.94	.5221	72.6	1.59	1.89
00040	21170.214	6.98	18.98	.5239	72.1	1.89	1.84
00041	21193.124	6.98	19.45	.5223	70.7	1.61	2.98
00042	21290.112	6.97	20.18	.5330	67.0	2.84	3.72
00043	21277.111	6.95	19.62	.5301	69.0	2.24	3.28
00044	21268.111	6.93	18.88	.5292	71.3	2.19	1.94
00045	21260.111	6.92	19.41	.5304	69.3	2.53	2.65
00046	21261.112	6.92	19.01	.5224	71.7	1.69	2.29
00047	21261.113	6.89	19.13	.5216	71.0	2.06	2.15

TABLE 1 (Continued)

00048	21275.123	6.89	19.34	.5207	70.5	1.65	3.05
00049	21145.123	6.87	19.91	.5392	66.3	3.47	3.36
00050	21180.114	6.85	20.93	.5216	65.2	1.80	6.29
00051	21275.122	6.85	20.01	.5156	68.5	2.08	3.63
00052	21271.111	6.84	18.18	.5257	73.5	1.57	1.49
00053	21170.212	6.83	18.93	.5268	70.5	2.40	2.07
00054	21258.212	6.82	18.65	.5316	70.9	2.14	2.30
00055	21301.113	6.75	18.53	.5045	74.1	1.49	.96
00056	21267.114	6.74	19.42	.5202	68.9	2.33	3.05
00057	21220.113	6.73	18.39	.5173	72.7	1.99	1.23
00058	21254.111	6.73	18.50	.5228	71.6	1.85	2.12
00059	21172.211	6.71	18.47	.5221	71.6	2.03	1.90
00060	21265.113	6.70	18.55	.5166	72.0	1.52	2.27
00061	21253.113	6.69	19.43	.5143	69.1	2.21	2.99
00062	21280.114	6.68	20.67	.5250	64.0	3.19	5.14
00063	21253.114	6.67	19.70	.5082	68.7	2.28	3.04
00064	21265.114	6.67	18.66	.5154	71.4	1.72	2.31
00065	21172.213	6.65	18.16	.5184	72.7	1.48	1.96
00066	21165.122	6.64	19.78	.5338	65.4	2.84	4.77
00067	21221.114	6.64	17.51	.5253	74.1	1.92	.73
00068	21278.111	6.64	20.74	.5038	65.8	2.69	4.29
00069	21165.124	6.62	19.28	.5393	66.1	3.08	4.03
00070	21300.114	6.61	21.34	.5160	62.6	2.43	7.21
00071	21267.111	6.60	18.78	.5159	70.3	2.05	2.53
00072	21220.112	6.59	17.87	.5185	73.2	1.86	1.21
00073	21260.113	6.59	18.23	.5230	71.2	1.93	2.24
00074	21301.111	6.59	18.14	.5179	72.2	1.97	1.58
00075	21170.211	6.57	18.86	.5219	69.0	2.16	3.20
00076	21254.112	6.56	18.09	.5250	71.2	2.27	1.87
00077	21295.112	6.53	20.91	.5275	62.0	3.71	5.93
00078	21281.113	6.52	20.45	.5263	63.2	3.78	4.88
00079	21262.113	6.51	18.39	.5158	70.8	2.10	2.18
00080	21278.113	6.51	20.87	.5122	63.5	2.55	6.30
00081	21281.112	6.51	20.61	.5267	62.7	3.67	5.40
00082	21290.113	6.50	19.60	.5301	65.2	3.16	4.45
00083	21277.112	6.44	18.43	.5265	68.7	2.17	3.43
00084	21253.112	6.42	19.05	.5256	66.4	3.47	3.07
00085	21281.114	6.42	21.33	.5288	60.0	4.09	6.93
00086	21262.114	6.40	19.21	.5209	66.4	2.31	4.62
00087	21266.111	6.39	18.57	.5109	69.5	2.42	2.40
00088	21170.121	6.38	17.65	.5203	71.8	1.89	1.95
00089	21173.212	6.36	18.35	.5115	70.0	1.93	2.80
00090	21270.111	6.32	16.90	.5239	73.6	1.69	1.27
00091	21254.113	6.31	18.16	.5243	68.7	2.66	2.80
00092	21266.113	6.31	18.26	.5141	69.5	2.25	2.72
00093	21265.111	6.25	17.61	.5174	70.9	2.02	2.26
00094	21220.114	6.18	18.77	.5216	65.6	3.87	3.01
00095	21259.124	6.18	16.88	.5234	72.2	2.21	1.38
00096	21170.122	6.11	18.02	.5092	69.0	2.32	2.84
00097	21221.113	6.10	16.35	.5239	73.6	1.82	1.18
00098	21266.112	6.07	18.39	.5133	66.8	2.57	3.88
00099	21280.113	6.07	20.37	.5231	60.2	4.20	6.52

TABLE 1 (Continued)

00100	21172.214	6.06	16.96	.5196	71.2	1.98	2.
00101	21186.113	6.06	19.71	.5098	63.1	3.41	5.
00102	21265.112	6.05	17.37	.5091	70.8	1.77	2.45
00103	21268.114	6.04	17.03	.5263	69.9	2.42	2.77
00104	21270.112	6.02	15.77	.5270	74.9	1.26	1.
00105	21288.113	5.95	18.79	.5311	62.6	4.13	4.88
00106	21288.114	5.93	18.79	.5313	62.4	4.05	5.14
00107	21266.114	5.91	17.68	.5152	67.5	2.63	3.
00108	21295.111	5.89	19.46	.5214	61.2	2.97	7.21
00109	21160.213	5.88	16.86	.5173	70.0	1.77	2.94
00110	21260.114	5.88	17.50	.5238	66.8	2.43	4.
00111	21290.111	5.87	17.58	.5254	66.3	2.68	4.
00112	21173.214	5.85	16.37	.5102	70.7	1.99	2.34
00113	21253.111	5.83	18.58	.5277	62.6	3.40	5.77
00114	21270.114	5.79	15.63	.5221	73.4	2.08	1.
00115	21275.121	5.79	18.08	.5083	65.7	2.24	4.60
00116	21173.213	5.68	15.62	.5221	72.2	1.95	1.69
00117	21268.112	5.67	15.82	.5284	70.5	2.47	2.
00118	21261.111	5.62	19.15	.5244	59.5	4.15	7.01
00119	21296.114	5.61	17.86	.5289	62.5	4.36	4.68
00120	21268.113	5.60	15.98	.5277	69.1	2.84	2.
00121	21262.112	5.57	18.01	.5268	62.0	4.00	5.
00122	21160.214	5.45	16.71	.5251	65.2	2.66	4.63
00123	21271.112	5.45	14.85	.5265	72.5	2.10	1.
00124	21173.211	5.42	15.94	.5078	69.7	2.07	2.
00125	21162.122	5.36	15.97	.5133	68.3	2.61	2.89
00126	21271.111	5.14	14.13	.5184	73.1	2.09	1.17
00127	21162.124	5.10	16.50	.5114	63.7	3.08	4.
00128	21283.112	5.09	15.77	.5116	66.2	3.00	3.57
00129	21279.112	5.08	18.54	.5030	58.2	3.29	8.58
00130	21173.123	4.95	14.80	.5091	68.7	2.93	2.3
00131	21283.114	4.93	15.83	.5187	63.5	3.77	4.4
00132	21179.124	4.92	13.87	.5095	72.5	2.42	1.00
00133	21173.121	4.91	14.74	.5119	68.2	2.87	2.
00134	21263.111	4.82	17.35	.5299	56.7	4.40	8.2
00135	21283.111	4.78	16.34	.5058	61.5	3.40	5.93
00136	21296.113	4.78	15.63	.5286	61.6	5.01	4.54
00137	21179.111	4.76	13.18	.5230	72.3	2.48	1.2
00138	21256.113	4.71	13.75	.5073	70.8	1.94	2.10
00139	21283.113	4.71	15.22	.5165	63.5	3.48	4.62
00140	21180.111	4.70	13.10	.5203	72.2	2.02	1.5
00141	21296.111	4.52	13.79	.5061	68.2	2.57	2.7
00142	21173.124	4.51	13.30	.5105	69.8	2.43	2.18
00143	21170.123	4.46	0.00	.0000	46.8	9.99	9.9
00144	21195.112	4.35	0.00	.0000	43.5	9.99	9.9
00145	21172.121	4.30	12.30	.5274	69.8	3.34	1.72
00146	21270.113	4.28	0.00	.0000	49.7	9.99	9.9
00147	21173.122	4.15	12.53	.5117	68.5	3.01	2.2
00148	21256.112	3.64	10.53	.5097	72.0	2.59	1.14
00149	21179.123	3.57	14.08	.4430	60.7	6.04	2.12

TABLE 1 (Continued)

00150	21296.112	3.53	0.00	.0000	53.8	9.99	9.99
00151	21180.112	2.99	15.74	.4181	54.2	7.29	3.09
00152	21146.114	2.44	7.60	.5334	65.6	6.10	1.94
00153	21146.111	2.33	7.42	.5309	64.7	5.09	2.31
00154	10457.114	2.22	0.00	.0000	26.2	9.99	9.99
00155	21147.111	2.04	6.29	.5245	68.0	5.78	1.28
00156	21170.114	2.04	5.90	.5235	72.2	2.53	.89
00157	21146.112	1.99	6.24	.5315	66.1	5.41	1.72
00158	21262.111	1.88	0.00	.0000	39.7	9.99	9.99
00159	21195.114	1.68	0.00	.0000	47.8	9.99	9.99
00160	21170.112	1.64	4.81	.5216	72.2	3.53	.68
00161	21172.124	1.61	0.00	.0000	25.3	9.99	9.99
00162	21300.111	1.53	0.00	.0000	28.4	9.99	9.99
00163	21226.112	0.73	0.00	.0000	24.8	9.99	9.99
00164	10456.124	0.61	0.00	.0000	23.2	9.99	9.99
00165	10457.113	0.55	0.00	.0000	20.0	9.99	9.99
00166	10456.122	0.34	0.00	.0000	24.6	9.99	9.99
00167	10457.112	0.28	0.00	.0000	23.5	9.99	9.99
00168	21179.112	0.19	0.00	.0000	25.1	9.99	9.99
00169	21300.113	0.14	0.00	.0000	25.3	9.99	9.99
00170	10456.121	0.13	0.00	.0000	24.8	9.99	9.99
00171	10456.123	0.09	0.00	.0000	25.1	9.99	9.99
00172	21279.111	0.03	0.00	.0000	24.9	9.99	9.99
00173	10457.111	0.01	0.00	.0000	24.4	9.99	9.99

A further 50 cells were made which had effectively zero efficiency due predominately to severe shorts or shunts.

(a)

(b)

FIGURE 2: Surface of electroformed copper foil after electrocleaning.
(a) Desired surface
(b) Region within dark spot visible under optical observation. Scanning electron micrographs X 5,000.

TABLE 2

Best eff. cell results for CdS substrates evaluated from 9/80 to 11/80.

EFF. RANK	SUBSTRATE #	MAX. CELL EFF.	$J_L/100\text{mW}$	V_{oc} at 25mA	FF	R_s	G_{SH}
00001	21195	8.41	22.24	.5180	74.2	1.22	1.48
00002	21193	8.28	22.16	.5202	73.1	1.48	1.73
00003	21301	8.09	21.63	.5113	74.4	1.24	1.18
00004	21276	7.94	21.63	.5239	71.6	1.65	2.45
00005	21179	7.86	21.10	.5190	73.3	1.45	1.69
00006	21278	7.73	22.21	.5256	68.0	2.22	3.95
00007	21170	7.66	20.67	.5201	72.8	1.74	1.49
00008	21220	7.59	21.38	.5189	70.0	2.20	2.45
00009	21271	7.54	20.10	.5239	73.2	1.72	1.38
00010	21263	7.46	20.80	.5268	69.8	2.34	2.50
00011	21258	7.44	20.54	.5289	70.3	2.13	2.60
00012	21259	7.42	20.73	.5319	69.1	2.44	2.89
00013	21260	7.41	20.46	.5315	70.0	2.21	2.71
00014	21300	7.26	21.10	.5080	69.6	1.83	3.23
00015	21267	7.21	20.10	.5236	70.4	2.09	2.50
00016	21261	7.12	19.19	.5259	72.5	1.72	1.87
00017	21290	7.09	20.99	.5265	66.3	3.13	3.59
00018	21277	7.01	19.69	.5241	70.0	2.09	2.79
00019	21268	6.93	18.88	.5292	71.3	2.19	1.94
00020	21275	6.89	19.34	.5207	70.5	1.65	3.05
00021	21180	6.85	20.93	.5216	65.2	1.80	6.29
00022	21254	6.73	18.50	.5228	71.6	1.85	2.12
00023	21265	6.70	18.55	.5166	72.0	1.52	2.27
00024	21253	6.69	19.43	.5143	69.1	2.21	2.99
00025	21280	6.68	20.67	.5250	64.0	3.19	5.14
00026	21221	6.64	17.51	.5253	74.1	1.92	.73
00027	21295	6.53	20.91	.5275	62.0	3.71	5.93
00028	21281	6.52	20.45	.5263	63.2	3.78	4.88
00029	21262	6.51	18.39	.5158	70.8	2.10	2.18
00030	21266	6.39	18.57	.5109	69.5	2.42	2.40
00031	21270	6.32	16.90	.5239	73.6	1.69	1.29
00032	21288	5.95	18.79	.5311	62.6	4.13	4.88
00033	21296	5.61	17.86	.5289	62.5	4.36	4.68
00034	21283	5.09	15.77	.5116	66.2	3.00	3.59
00035	21279	5.08	18.54	.5030	58.2	3.29	8.58
00036	21256	4.71	13.75	.5073	70.8	1.94	2.10
00037	21146	2.44	7.60	.5334	65.6	6.10	1.94
00038	10457	2.22	0.00	.0000	26.2	9.99	9.99
00039	21147	2.04	6.29	.5245	68.0	5.78	1.28
00040	21226	0.73	0.00	.0000	24.8	9.99	9.99
00041	10456	0.61	0.00	.0000	23.2	9.99	9.99
00042	21297	0.00	0.00	.0000	0.0	9.99	9.99

Development of $\text{Cu}_2\text{S}/\text{CdS}$ Device on 7059 Glass

Preliminary work has been started on the design and fabrication of a $\text{Cu}_2\text{S}/\text{CdS}$ cell on a transparent substrate. The basic structure of the device consists of:

- 1) A Corning 7059 glass substrate,
- 2) a transparent contact layer to the CdS,
- 3) CdS layer,
- 4) Cu_2S layer, and
- 5) a Cu_2S contact which will be either a transparent metal grid or a continuous metal film (permitting backwall cell operation only.)

The device with a transparent contact to the Cu_2S can be illuminated from either the CdS or Cu_2S side and will be an extremely valuable tool for analysis.

The following criteria have been set for an acceptable CdS contact layer;

- 1) The material must make good ohmic contact to the CdS and be chemically and electronically stable.
- 2) Transmission through the material in the 400-1200nm range should be greater than 80%.
- 3) The series resistance contribution to the device should be less than $0.5 \Omega\text{-cm}^2$.

Two types of contacts that can meet those criteria are being pursued - a conductive oxide (only ITO, to date) and a metallic grid structure.

To use a conductive oxide, a sheet resistance of less than $10 \Omega/\square$ is required for a 1 cm^2 cell.

Corning 7059 glass slides have been sputter coated with ITO. The ITO target is badly cracked and reproducibility and film integrity has been poor. The best films prepared with good transmission have a sheet resistance of approximately $20 \Omega/$.

The use of a transparent grid for the CdS contact requires a parallel line grid pattern with ~ 16 line/cm and 25 micron line width for a CdS sheet resistance of $10^3 \Omega/$ and a grid material resistivity of less than $6 \times 10^{-6} \Omega\text{-cm}$. A 16 line/cm zinc grid has been deposited on 1" x 1" 7059 slides. Differences in the CdS covering the zinc grid and the bare glass have been noted and will be discussed later.

CdS has been deposited on 7059 glass substrates with and without a contact layer. The temperature of the glass substrate is controlled by a thermocouple imbedded in the front surface (CdS side) of the slide which is radiatively heated from the back. The CdS films made to date have the following characteristics:

- 1) The adherence of the CdS is excellent for the ITO coated slides, but can be a problem on gridded and bare slides.
- 2) The CdS resistivity is in the desired 1 to $20 \Omega\text{-cm}$ range.
- 3) The grain structure is generally similar to CdS grown on copper foil, but with a smaller grain size. (See Figure 3.)
- 4) The x-ray diffraction pattern of the film is similar to CdS grown on the copper foil, showing a strongly preferred (0001) orientation.
- 5) The photoluminescence has both the exciton (490nm) and edge emission ($\sim 520\text{nm}$) peaks. No other peaks have been observed.

The Cu_2S layer has been formed by the solution process. Samples with an ITO contact layer could be processed in the same manner as our standard material. Samples with no contact layer or with a grid had to be slowly preheated prior

to the barrier step to prevent the CdS spalling off the glass substrate. This reflects the poor adherence of the CdS to the glass coupled with thermal shock. Measurements of Cu₂S thicknesses have not yet been made.

The total reflectance, transmission and absorptance were measured for Cu₂S/CdS/ITO/7059 glass and the average solar reflectivity, $\bar{R}$, transmission, $\bar{T}$, and absorptance, $\bar{A}$, for AM 1.5 in the 0.40 to 1.00 μm range were calculated. For a 10 second barrier, $\bar{R} = 0.325$, $\bar{T} = 0.242$ and $\bar{A} = 0.433$. A more detailed optical analysis of the multilayer structure will be made.

Several cells have been fabricated using both ITO and zinc grids, and tested in the frontwall mode of operation without back surface reflection. The efficiencies were all less than 1% and devices suffered from various processing or design problems. The major problem now being addressed is the back contact.

On devices with ITO contacts, the sheet resistance was high and the integrity of the ITO was questionable. A new ITO target is being purchased and should arrive during February. Substrates with commercially prepared ITO have been obtained and will also be tested.

The cells with the zinc grid contact to the CdS, exhibit an unusual behavior. The cell area above the zinc grid appears to be completely inactive, and this was confirmed by laser scanning the device. Figure 4 shows that virtually no current is measured in the areas directly above the zinc grids. The CdS grown on zinc grid lines appears to be different than to that on the glass. This probably results from a local temperature difference of the grid line and the glass during CdS growth. Since the emissivity of the glass, ~ 0.9 , is much higher than zinc, 0.5 (unoxidized at 300°C,) the grid line would tend to be at a higher temperature than the glass. The

FIGURE 3: SEM of CdS grain structure on 7059 glass substrate. Mag. $\times 5000$.

FIGURE 4: Laser scan images of $\text{Cu}_2\text{S}/\text{CdS}$ cell on 7059 glass with 16 line/cm zinc grid contacting the CdS running horizontally and a 31 line/cm gold grid contacting the Cu_2S running vertically. Amplitude modulated scan in 0.8V reverse bias.

thermal conductivity of the glass is poor and a temperature gradient could be maintained. A similar effect has also been reported by Telic. Experiments to confirm this analysis are currently in progress.

In the next quarter, the performance of the device should be greatly improved and final design of the device established. A temperature controlled mount for testing these devices will also be designed and built.

Alternate Grid Structure

A new technique for gridding devices has been developed and implemented. The main feature of the new technique is a combined magnet-vacuum chuck. The $\text{Cu}_2\text{S}/\text{CdS}$ sample is first held flat by a vacuum drawn through a perforated sheet of Plastiform magnet. The grid mask is then applied and held in intimate contact to the sample by the Plastiform magnet and a mechanical hold-down. The vacuum is then released and the mounting fixture and sample are placed in the turret e-gun vacuum system for gold deposition. It is believed that this new technique will solve the problem encountered with the multilayer, gold-nickel-copper grid structure reported in Reference 1. With the previous system, sagging of the evaporation mask during copper deposition resulted in the copper contacting the Cu_2S beyond the gold/nickel layer. Evaluation of the multilayer structure using the improved technique will take place during the next quarter.

A method of evaluating the contact properties of materials other than gold to Cu_2S is also being developed. The approach is to deposit an interdigitated grid structure on a $\text{Cu}_2\text{S}/\text{CdS}$ device with alternating grid materials. One of the materials will always be gold and act as a reference contact. The device characteristics for

the gold grid and the new material grid can be independently measured and compared. Additionally, the contact characteristics of the new material relative to the gold can be directly evaluated by measuring the I-V characteristics between the two grids. A grid-mask system is being designed for depositing the interdigitated materials.

4.2 Cu₂S/CdS CELL PRODUCTION

80 Cu₂S/(CdZn)S cells were made during this reporting period. Figure 5 shows a histogram of efficiency. Table 3 lists the cells in descending efficiency. Nine new substrates were made during the quarter, and the best cell from each substrate is listed in Table 4. The generally poor yield is believed to be related in part to the problems discussed in Section 4.1.

Close inspection of the defects in Cd_{1-x}Zn_xS film grown on copper that are revealed by the Cu₂S/KCN technique⁽²⁾ indicates that, in addition to the normal observed grain boundaries, there are linear defects having distinct ends suggesting microcracks. (See Figure 6.) Inspection indicates an absence of these kinds of film defects for Cd_{1-x}Zn_xS (x = 0.11) deposited on NiFe (1-347) (See Figure 7.) A further indication of these crack defects is revealed by the SEM micrographs of the textured-only surface of samples from the same Cd_{1-x}Zn_xS film (x = .23, 1-353) depicted in Figure 6. Figure 8 shows the micrograph of the surface textured by immersion in a 60°C, 25% HCl standard texturing solution for a) 20 seconds and b) 40 seconds. This figure shows elongated etch pits which grow in width with increasing texture time. Figure 9 shows Cd_{1-x}Zn_xS deposited on NiFe (from the same film as used for Figure 7) which had been textured for 40 seconds in the standard texture solution. There are no elongated etch pits, although there are some circular etch pits perhaps resulting from Cd_{1-x}Zn_xS grains which have popped out of the film either prior to, or as a consequence of, the texturing. Figures 10 and 11 show the SEM micrographs of the surfaces of the wet-process Cu₂S/Cd_{1-x}Zn_xS cells prepared on copper (1-353-113) and NiFe (1-347-113), respectively. The former cell was textured for 15 seconds, the latter for 20 seconds. The Cu₂S/Cd_{1-x}Zn_xS cell on the copper substrates shows

MIDDLE OF INTERVAL	NUMBER OF OBSERVATIONS	# OF CELLS
EFF. 0.0	45	*****
0.5	2	**
1.0	2	**
1.5	0	
2.0	0	
2.5	0	
3.0	2	**
3.5	0	
4.0	0	
4.5	1	*
5.0	0	
5.5	6	*****
6.0	1	*
6.5	3	***
7.0	0	
7.5	2	**
8.0	2	**
8.5	2	**
9.0	6	*****
9.5	3	***
10.0	3	***

FIGURE 5: Histogram of 80 $\text{Cu}_2\text{S}/(\text{CdZn})\text{S}$ cells made during September through November, 1980.

TABLE 3

Cu₂S/(CdZn)S cells made from 9/80 to 11/80 ranked with respect to Eff.

Eff. RANK	CELL #	MAX. EFF.	J _L /100mW	V _{oc} at 25mA	FF	R _s	G _{SH}
00001	10423.114	10.16	22.78	.5843	77.3	1.06	.89
00002	10423.112	9.77	22.26	.5845	76.1	1.48	.89
00003	10423.113	9.77	22.43	.5814	76.0	1.20	1.37
00004	10418.123	9.65	22.61	.5783	74.9	1.67	1.21
00005	10418.124	9.50	21.55	.5859	76.4	1.29	1.07
00006	10423.111	9.38	22.16	.5636	76.2	1.25	.95
00007	10434.113	9.22	22.00	.5855	72.9	2.07	1.89
00008	10423.123	8.99	21.50	.5665	75.1	1.63	1.04
00009	10423.121	8.92	21.18	.5665	75.6	1.28	1.27
00010	10423.124	8.90	21.23	.5666	75.2	1.52	1.13
00011	10423.122	8.79	20.99	.5691	74.9	1.46	1.43
00012	10434.112	8.75	22.72	.5856	67.6	2.52	4.46
00013	10418.121	8.54	20.26	.5984	72.2	1.70	2.84
00014	10353.211	8.49	21.35	.6045	67.8	2.78	4.13
00015	10418.213	8.18	18.48	.5905	76.6	1.42	.93
00016	10418.214	7.80	17.89	.5925	75.5	1.59	1.27
00017	10419.121	7.70	17.28	.6110	75.0	1.55	1.67
00018	10418.211	7.59	18.77	.5692	72.9	2.14	1.70
00019	10353.214	6.61	14.98	.6209	73.6	2.22	1.71
00020	10418.111	6.58	17.02	.6024	66.8	1.86	4.71
00021	10353.212	6.38	14.83	.6211	71.9	2.52	2.14
00022	10392.121	5.75	16.00	.6015	63.1	6.01	3.67
00023	10405.123	5.73	14.69	.6006	68.0	3.82	2.78
00024	10405.124	5.69	14.43	.5968	69.1	3.67	2.42
00025	10392.122	5.57	14.99	.6008	65.2	4.99	3.32
00026	10405.121	5.54	15.04	.5873	65.8	5.36	2.64
00027	10405.122	5.53	14.58	.5965	66.7	5.10	2.54
00028	10392.124	5.44	15.37	.6029	62.3	6.68	3.64
00029	10418.112	4.57	17.37	.4986	56.9	6.22	6.05
00030	10438.114	2.88	7.12	.6450	67.6	6.29	1.67
00031	10438.112	2.82	7.38	.6472	64.1	8.00	2.16
00032	10435.114	1.24	0.00	.0000	38.4	9.99	9.99
00033	10435.112	1.04	0.00	.0000	35.4	9.99	9.99
00034	10418.114	0.53	0.00	.0000	29.2	9.99	9.99
00035	10353.213	0.30	0.00	.0000	25.0	9.99	9.99

A further 45 cells were made which were either severely shunted giving effectively zero efficiency or had I-V curves showing hysteresis.

TABLE 4

Best eff. cell results for (CdZn)S substrates evaluted from 9/80 to 11/80.

RANK EFF.	SUBSTRATE #	MAX. CELL EFF.	J _L /100mW	V _{oc} at 25mA	FF	R _s	C _{SH}
00001	10423	10.16	22.78	.5843	77.3	1.06	.89
00002	10418	9.65	22.61	.5783	74.9	1.67	1.21
00003	10434	9.22	22.00	.5855	72.9	2.07	1.89
00004	10419	7.70	17.28	.6110	75.0	1.55	1.67
00005	10438	2.88	7.12	.6450	67.6	6.29	1.67
00006	10435	1.24	0.00	.0000	38.4	9.99	9.99
00007	10421	0.06	0.00	.0000	25.2	9.99	9.99
00008	10431	0.03	0.00	.0000	25.0	9.99	9.99
00009	10422	0.00	0.00	.0000	0.0	9.99	9.99

the presence of substantially more crack defects, than observed for the cell prepared on the NiFe substrate. We have reported⁽³⁾ that $\text{Cu}_2\text{S}/\text{Cd}_{1-x}\text{Zn}_x\text{S}$ devices prepared on NiFe are more stable than $\text{Cu}_2\text{S}/\text{Cd}_{1-x}\text{Zn}_x\text{S}$ devices on copper.

The indication of crack defects revealed by the $\text{Cu}_2\text{S}/\text{KCN}$ technique is more readily evidenced in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films with higher zinc content ($x \geq 0.3$). Figure 12 shows defects in the surface of a $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .36$ #1-392) film (0 texture, 16s CuCl .) Cracks are clearly evident although only slight attack has occurred at the grain boundaries. It has been shown⁽²⁾ that the rate of Cu_2S formation at grain boundaries decreases with increasing zinc concentration. For example, to reveal grain structure it takes 6 seconds for CdS compared to 16 seconds for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($0.1 < x < 0.2$). Figure 13 shows that the surface of the same substrate described in Figure 12, reveals the grain boundaries after 48 seconds reaction in CuCl .

Figure 14 shows the surface of samples from the above substrate, textured (60°C , 25% HCl) for a) 20 seconds, and b) 40 seconds. Clearly evident are elongated cracks which get wider with increased texturing time. Figure 15 shows the SEM micrograph of the surface of a cell made from this substrate. (20s texture, 15s CuCl) in which grain size cracks are quite clear.

The severity of crack defects is clearly enhanced by surface texturing (Figure 14), and consequently the morphology of wet-process Cu_2S will be characterized by deep intrusions. The effect of these crack intrusions will be to reduce the open circuit voltage and to provide a source for the formation of shunts due to copper migration. The latter will lead to voltage instability. In accord with the first effect, the open circuit voltages of cells prepared on substrate #1-392 were low ($.59 < V_{oc} < .63$), despite the high zinc concentration ($x = 0.36$).

FIGURE 6: SEM micrograph of grain revealed $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .23$) film (1-353) deposited on copper. X 2000.

FIGURE 7: SEM micrograph of grain revealed $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .11$) film (1-347) deposited on NiFe. X 2000.

(a)

(b)

FIGURE 8: SEM micrograph of surface textured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .23$) film (1-353) deposited on copper. The texture times were a) 20 seconds, and b) 40 seconds. X 2000.

FIGURE 9: SEM micrograph of surface textured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .23$) film (1-353) deposited on NiFe. The surface was textured for 80 seconds. X 2000.

FIGURE 10: SEM micrograph of Cu_2S cell (1-353-113) prepared on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x=.23$) film deposited on copper. The texture time was 15 seconds. X 2000.

FIGURE 11: SEM micrograph of Cu_2S cell (1-347-113) prepared on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .11$) film deposited on NiFe. The texture time was 20 seconds. X 2000.

FIGURE 12: SEM micrograph of defect revealed surface of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .36$) film (1-392) deposited on copper. Defects revealed by immersion in standard CuCl solution for 16 seconds and KCN stripped. X 2000.

FIGURE 13. SEM micrograph of defect (i.e., cracks plus grain boundaries) revealed surface of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x=.36$) film (1-392) deposited on copper. Defects revealed by immersion in standard CuCl solution for 48 seconds and KCN stripped. X 2000.

(a)

(b)

FIGURE 14: SEM micrograph of surface textured $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($X = .36$) film (1-392) deposited on copper. The texture times were a) 20 seconds, and b) 40 seconds. X 2000.

FIGURE 15: SEM micrograph of Cu_2S cell (1-3920224) prepared on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = .36$) deposited on copper. X 2000.

As was previously indicated, the extent of the bimodal distribution of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ grain sizes was greatly reduced following several systematic changes in the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ growth system⁽³⁾. The initial suggestion that this was due to a change in source of ZnS has been found to be in error. Recent investigations have shown that the extent of the small grain regions of the bimodal distribution is related to the substrate temperature⁽²⁾. An improved temperature control procedure utilizing a thermocouple directly spot-welded to the substrate provided the necessary reproducibility of substrate temperature and conditions eliminating the bimodal structure can now be routinely attained.

A preliminary design of an alternative source for the deposition of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films utilizing three separate sources of cadmium, zinc and sulfur is being evaluated. A major advantage to this approach is the fact that all three components will be in the liquid state, simplifying the measurement and control of the actual temperature of the source materials⁽⁴⁾.

4.3 CELL ANALYSIS

During this period, the laser spot scanner has been configured so that it can be used on ungridded Cu_2S material to detect shorting defects. The ungridded material is pressure contacted on one side with a conductive silicone rubber. To eliminate series resistance effects, the sample is held in reverse bias (-0.5V.) Shorted areas show up as "holes" in the response. Figure 16 shows the response of a relatively uniform cell with little evidence of shorts or shunts. In contrast, Figure 17 shows a number of severe "drop outs" indicative of localized shorting. Such imaging is not possible with conventionally gridded cells.

Improved optical and signal processing is planned to achieve better resolution and discrimination.

FIGURE 16: Laser scan of ungridded cell #10423.214 with pressure contacts at -0.5V bias, showing a relatively uniform response.

FIGURE 17: Laser scan of ungridded cell #10422.121 with pressure contacts at -0.5V bias, showing a large density of shorts.

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APPENDIX

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