CdS THIN FILM SOLAR CELLS FOR TERRESTRIAL POWER

Grant No. AER74-14918

Westinghouse Research Laboratories

ABSTRACT

The overall objective is the development of very low cost long lived Cu_2S/CdS thin film solar cells for large scale energy conversion. This review covers approximately the second half of the first year's work at Westinghouse.

In this period, the facility for fabricating a modified design terrestrial cell was operated steadily. Cell outputs started out low (at 3.4%), dropped (to 2.0%) when closer controls were placed on the process, increased (to 3.4%) when a revised rinsing process was introduced, and increased further (to 5.0% average) when a revised barrier forming process was put into effect.

Work continued on the development of a low cost grid system. A printed grid, using flake graphite pigment in a polysulfone binder was developed, and gave reasonably compatible grid lines. However, the line width and resistivity were both too high for the required fine mesh grid and further work was postponed.

Excellent evaporated metal grid patterns were obtained using a specially designed aperture mask. Line widths of 1 mil and spacings of 50 and 100 lines per inch were readily obtained. Vacuum evaporated gold and copper grids of 50 lines per inch and 1 micron thickness were adequate electrically for the fine mesh contacting grid. Some difficulty was encountered with such grids dropping cell output to half or less, though usually the outputs could be restored by vacuum annealing. The difficulty is believed to be due to localized shorting of the grid to n-type CdS in crevices in the Cu_2S layer.

Real time roof top sunlight exposure tests of encapsulated

CdS cells show no loss in output after 5 months.

Accelerated life testing of encapsulated cells show no loss of output power after 6 months of 12 hour dark-12 hour AM1 illumination cycles at 40°C, 60°C, 80°C and 100°C temperatures. However, the cells are showing changes in their basic parameters, such as series and shunt resistance and junction capacitance. There are indications that these changes can be correlated with specific degradation modes and hence there is an expectation that the accelerated tests will be of value in predicting cell lifetimes in normal usage.

A- CdS THIN FILM SOLAR CELLS FOR TERRESTRIAL POWER

GRANT NO. AER74-14918

BY

WESTINGHOUSE ELECTRIC CORPORATION
RESEARCH LABORATORIES
PITTSBURGH, PENNSYLVANIA

WITH

THE UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

PERIOD OF GRANT AUGUST 1, 1974 THRU JULY 31, 1975
AMOUNT OF GRANT $247,200
PRINCIPAL INVESTIGATOR - F. A. SHIRLAND

B- OVERALL OBJECTIVE OF PROJECT

THE DEVELOPMENT OF VERY LOW COST LONG LIVED CdS/Cu_2S THIN FILM SOLAR CELLS

THE FIRST PHASE OF A THREE YEAR EFFORT TO CARRY THE CdS THIN FILM SOLAR CELL TO THE THRESHOLD OF PRACTICAL APPLICATIONS

C- PLANNED ACTIVITY FOR LAST SIX MONTHS

1- SOLVE PROBLEM OF HIGH R_S AND LOW SCC
2- OPERATE STANDARD PROCESS CELL FABRICATION FACILITY AND ACHIEVE 4% MINIMUM EFFICIENCY LEVEL
3- CONTINUE DEVELOPMENT OF LOW COST GRID SYSTEM
4- STUDY METHODS OF PROTECTING CELLS FROM THE ATMOSPHERE-RECOMMEND APPROACH FOR INTENSIVE DEVELOPMENT
5- OBTAIN FIRST INDICATIONS OF EXPECTED LIFETIMES OF STATE-OF-THE-ART CELLS IN TERRESTRIAL USE
6- START BASIC STUDIES OF CELL STRUCTURE AND OPERATING MECHANISM
7- START STUDIES OF Cu_2S LAYER TO OPTIMIZE STRUCTURE FOR THINNER BASE LAYERS
8- ANALYZE LOSSES IN STATE-OF-THE-ART CELLS TO DEMONSTRATE PRACTICALITY OF HIGHER CELL EFFICIENCIES

D- DESCRIPTION OF PROGRESS MADE

1. PROBLEM OF HIGH R_S AND LOW SCC

HIGH R_S VALUES EARLIER WERE APPARENTLY DUE TO INADEQUATELY FORMED JUNCTIONS. THEY IMPROVED GREATLY WHEN BETTER JUNCTIONS WERE WERE MADE.

HIGHER CURRENTS (15 TO 19 MA/CM^2) WERE OBTAINED BY INCREASED ETCH TO OPEN GRAIN BOUNDARIES, AND BY USE OF HIGHER CuCl DIP TEMPERATURE

D- DESCRIPTION OF PROGRESS MADE

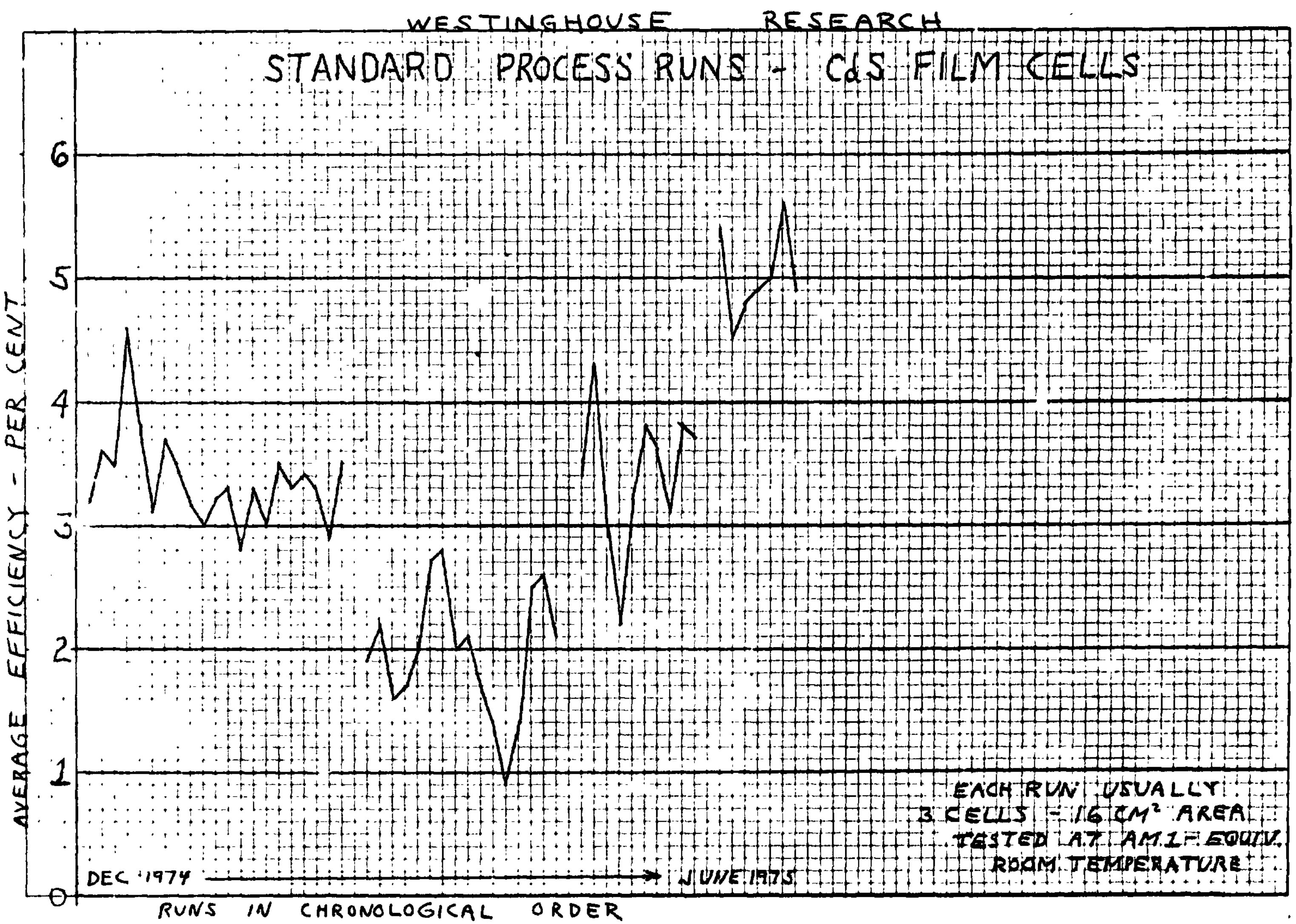
2- STANDARD PROCESS CELL FABRICATION

A TOTAL OF 53 STANDARD PROCESS CELL RUNS MADE IN
6 MONTH PERIOD (3 CELLS/RUN)

INITIAL PROCESS	AVG. EFF.	=	3.4%
TIGHTENED CONTROLS	AVG. EFF.	=	2.0%
REVISED PROCESS - FASTER RINSE	AVG. EFF.	=	3.4%
RE-REVISED PROCESS - NEW ETCH + DIP	AVG. EFF.	=	5.0%

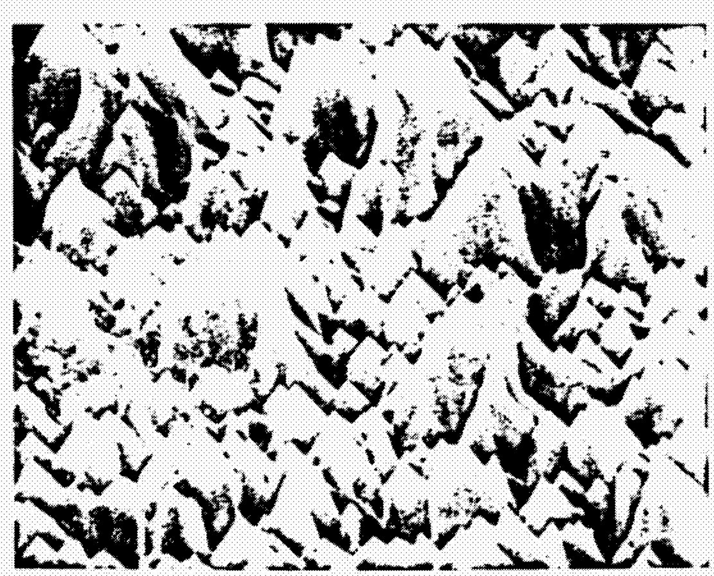
REPRODUCIBILITY - FAIR (± 20% AT 5.0% LEVEL)

YIELD - GOOD 87% IN 3RD QTR.
92% IN 4TH QTR.


WESTINGHOUSE RESEARCH
STANDARD PROCESS RUNS - CdS FILM CELLS
AVERAGE EFFICIENCY - PER CENT
0
1
2
3
4
5
6
DEC 1974
JUNE 1975
RUNS IN CHRONOLOGICAL ORDER
EACH RUN USUALLY
3 CELLS - 1.6 CM² AREA
TESTED AT AM1 EQUIV.
ROOM TEMPERATURE

→| |←1 μ

RUN 97-5000X (Old Process)



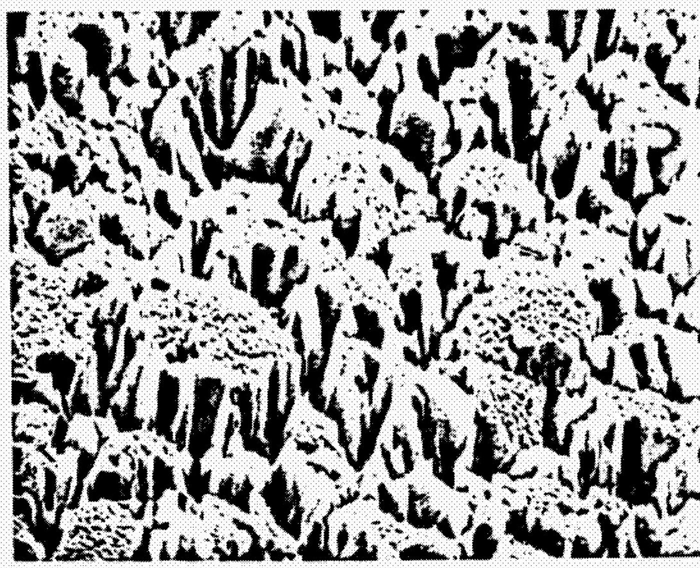
Run 189-5000X (New Process)

ORIGINAL PAGE IS
OF POOR QUALITY

SEM PICTURE OF SURFACE OF
Cu_2S/CdS CELL

(5000X)

→||← 1 μ



Run 97-2000X (Old Process)

Run 185-2000X (New Process)

SEM PICTURE OF SURFACE OF
Cu_2S/CdS CELL

(2000X)

D- DESCRIPTION OF PROGRESS MADE

3- LOW COST GRID SYSTEM

DUAL GRID SYSTEM SELECTED AS MOST PROMISING
- FINE GRID CONTACT - EVAPORATED OR PRINTED
- COARSE COLLECTOR BUS - METALLIC OVERLAY

PRINTED GRID - FLAKE GRAPHITE PIGMENT, POLYSULFONE BINDER
- RESISTIVITIES WERE TOO HIGH
- RESOLUTIONS WERE TOO LOW

EVAPORATED GRID - MECHANICS OF PROCESS WORKED OUT
- APERTURE MASKS - 1 MIL LINE WIDTHS
  - 50 LPI SPACING UP TO 100
- EXCELLENT PATTERNS OBTAINED - GOOD ADHESION & COND.
- EVAPORATED METALS REDUCE CELL OUTPUT

COARSE COLLECTOR GRID - CONDUCTIVE EPOXY INTERCONNECT - OK
- THERMO-COMPRESSION BONDING - NOT TRIED

D- DESCRIPTION OF PROGRESS MADE

3- LOW COST GRID SYSTEM

PRINTED GRID

PROBLEM:

ORDINARY CONDUCTIVE INKS - MUCH TOO HIGH RESISTANCE

ANALYSIS

PIGMENT SURFACE AREA TOO HIGH TO OBTAIN HIGH LOADING

APPROACHES

A- FLAKE PIGMENT TO REDUCE SURFACE AREA & INCREASE PARTICLE TO PARTICLE CONTACTS

FLAKE GRAPHITE EVALUATED

RESULTS PROMISING - BUT STILL TOO HIGH IN RESISTANCE -- TOO COARSE FOR DESIRED RESOLUTION

FLAKE COPPER MAY HELP

B- CONDUCTIVE BINDER

C- IMPROVED MIXING TO PREVENT COMPLETE WETTING OF PIGMENT

D- DESCRIPTION OF PROGRESS MADE

3- LOW COST GRID SYSTEM

EVAPORATED GRID

PROBLEM:

AFTER GRID IS EVAPORATED, CELL OUTPUT (OCV + EFF.) DROPS.

ANALYSIS:

EVAPORATED METAL PROBABLY SHORTING TO CDS IN GRAIN BOUNDARY CREVICES

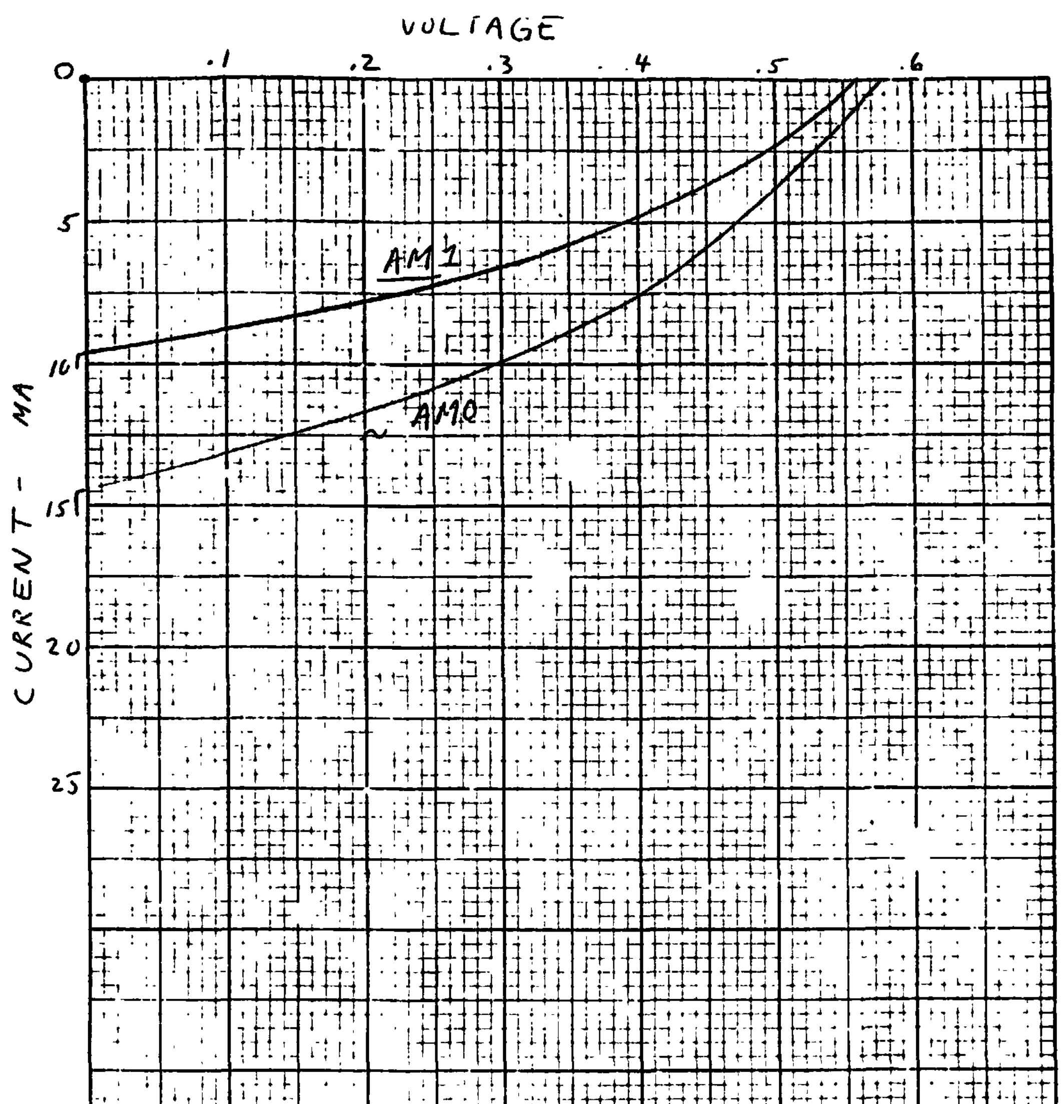
APPROACHES:

A- DIFFERENT METALS
VARIOUS METALS HAVE BEEN TRIED. GOLD WORKS BEST, AND COPPER NEXT. MAY TEND TO FORM BLOCKING CONTACT. (AFTER AU OR CU GRID EVAPORATION, OUTPUT OF CELL CAN USUALLY BE RESTORED BY VACUUM ANNEALING.) TRY GRAPHITE.

B- P^+ SEMI-CONDUCTOR UNDER METAL ELECTRODE. (Cu_2S, SI, SE)
Cu_2S REACTIVELY SPUTTERED-GAVE GOOD JUNCTION TO CDS

C- OBLIQUE EVAPORATION TO MINIMIZE PENETRATION IN CREVICES

D- IMPROVE CONTINUITY OF Cu_2S BARRIER LAYER
LONGER CUCL DIP TIME-WEAKER BATH
IMPROVED AGITATION DURING DIPPING
SLOWER ETCH TO REDUCE CREVICING
FORM Cu_2S BARRIER BY SOLID STATE DIFFUSION



Run: 16P-210 Date: 6/6/75 Area: 4 (cm^2) Oper:

V_{OC}(V)	.558	J_{SC}(mA/cm^2)	2.5
I_{SC}(A)	.0095	P_M(W)	.00200
I_{MP}(A)	.0055	η(%)	0.5 %
V_{MP}(V)	.364	F.F.(%)	37 %
R_{SH}(Ω)	2510	R_S(Ω)	20
ρ_{SH}($Ω/cm^2$)	10^4	ρ_S($Ω/cm^2$)	80

Comments:

SPUTTERED Cu_2S BARRIER LAYER

D- DESCRIPTION OF PROGRESS MADE

4- PROTECTING CELLS FROM ATMOSPHERE

R.F. SPUTTERING SYSTEM OBTAINED, SET-UP AND TOOLED

SiO_2, Al_2O_3, AND Si_3N_4 TARGETS OBTAINED

SiO_3, Al_2O_3 AND Si_3N_4 SPUTTERED ONTO GLASS - TO CALIBRATE PROCESS

GOOD ADHERENT, PINHOLE-FREE COATINGS OBTAINED 0.2 TO 1.0μ THICK

READY TO APPLY TO Cu_2S LAYER CELLS

D- DESCRIPTION OF PROGRESS MADE

5- LIFE TESTING

A- ROOF-TOP TEST

5 MONTHS REAL TIME EXPOSURE - NO LOSS OF OUTPUT

B- ACCELERATED LIFE TEST

IN-SITU OUTPUT MEASUREMENTS FOR 6 MONTH ACCELERATED EXPOSURE

SOME INITIAL DROPS, BUT MOST CELLS HOLDING UP

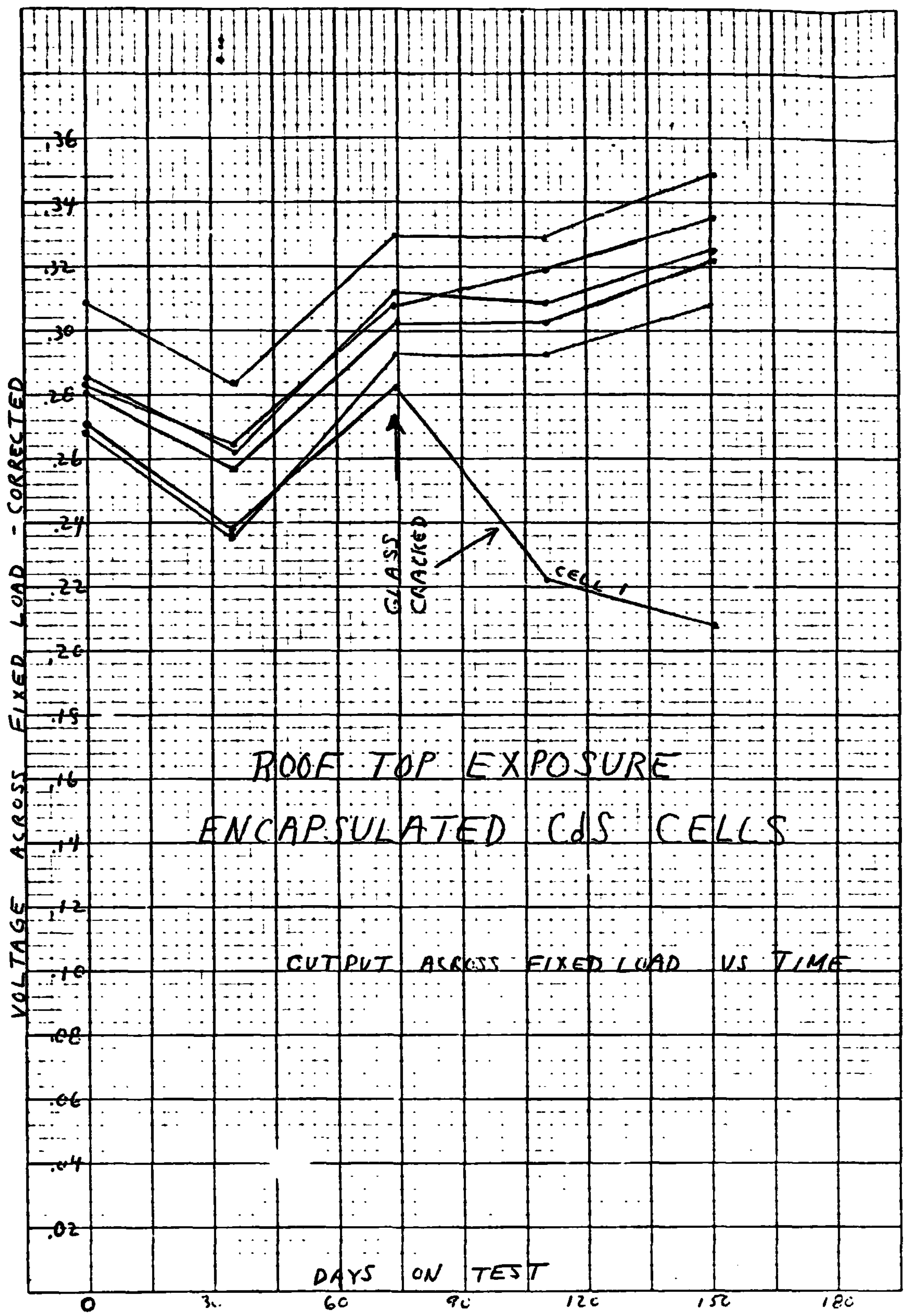
ACCURATE SIMULATOR TEST BEFORE & AFTER 6 MONTHS ACCELERATED EXPOSURE

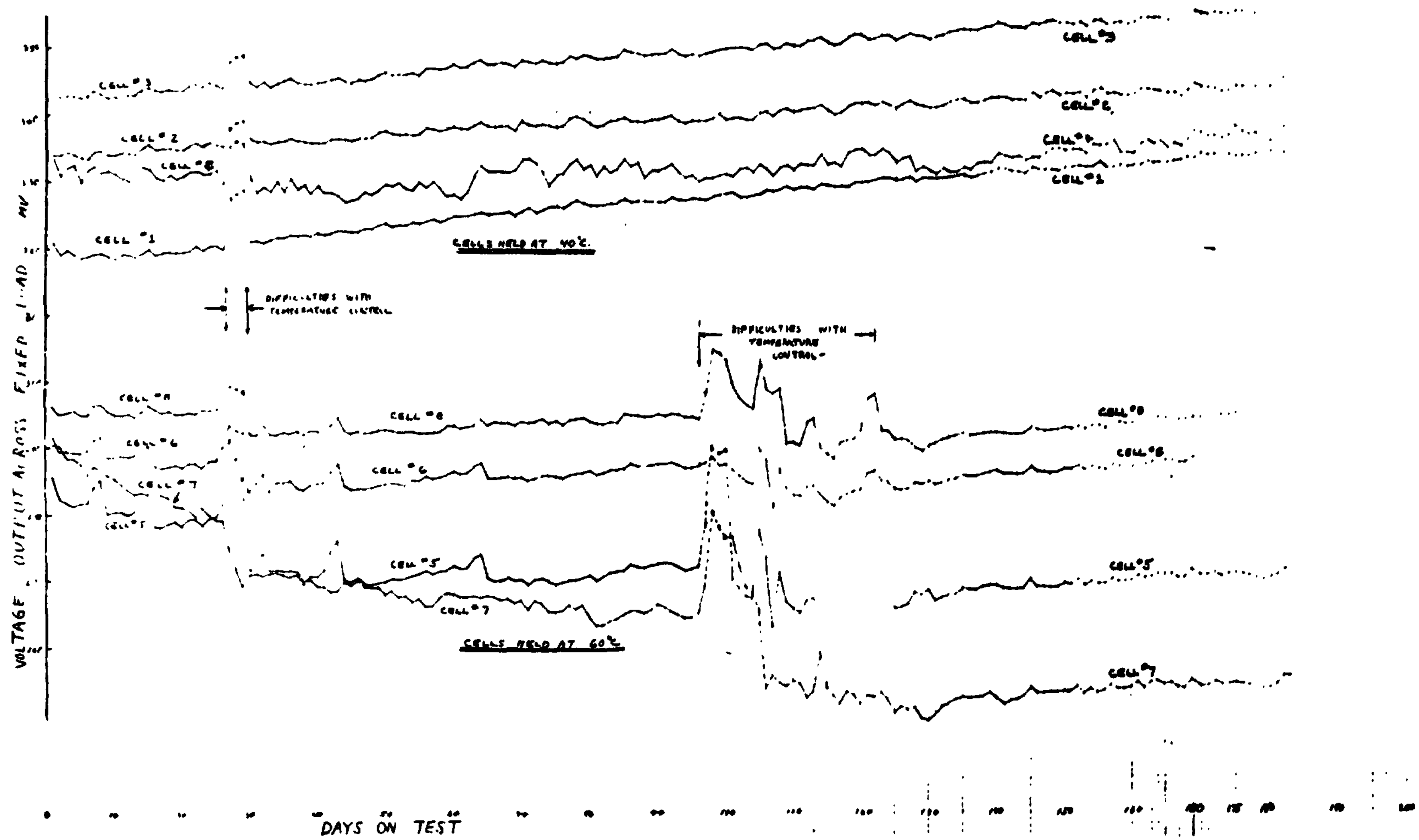
MOST CELLS SHOWING NO LOSS OF OUTPUT

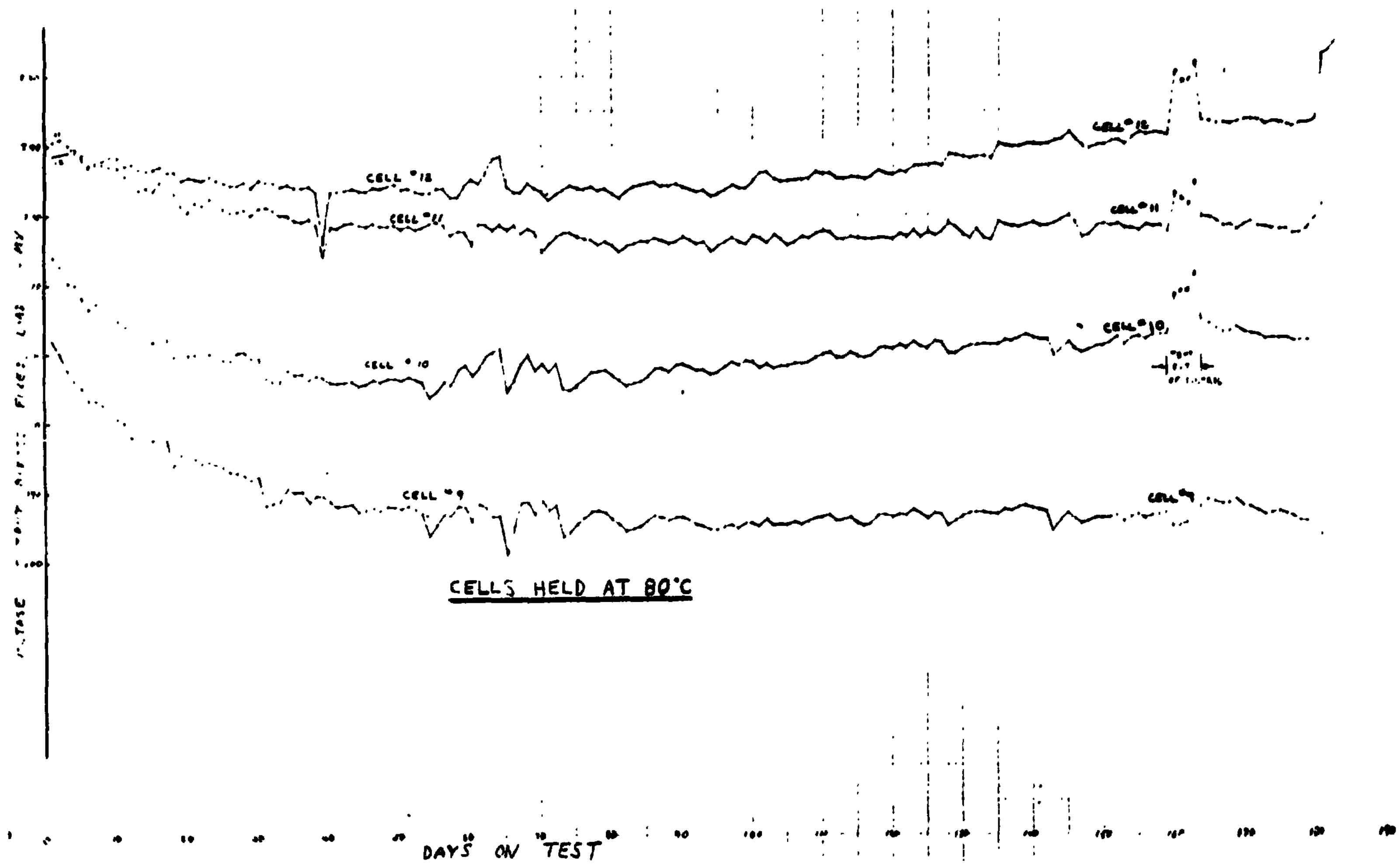
INTERNAL CELL PARAMETERS SHOWING SOME CHANGES

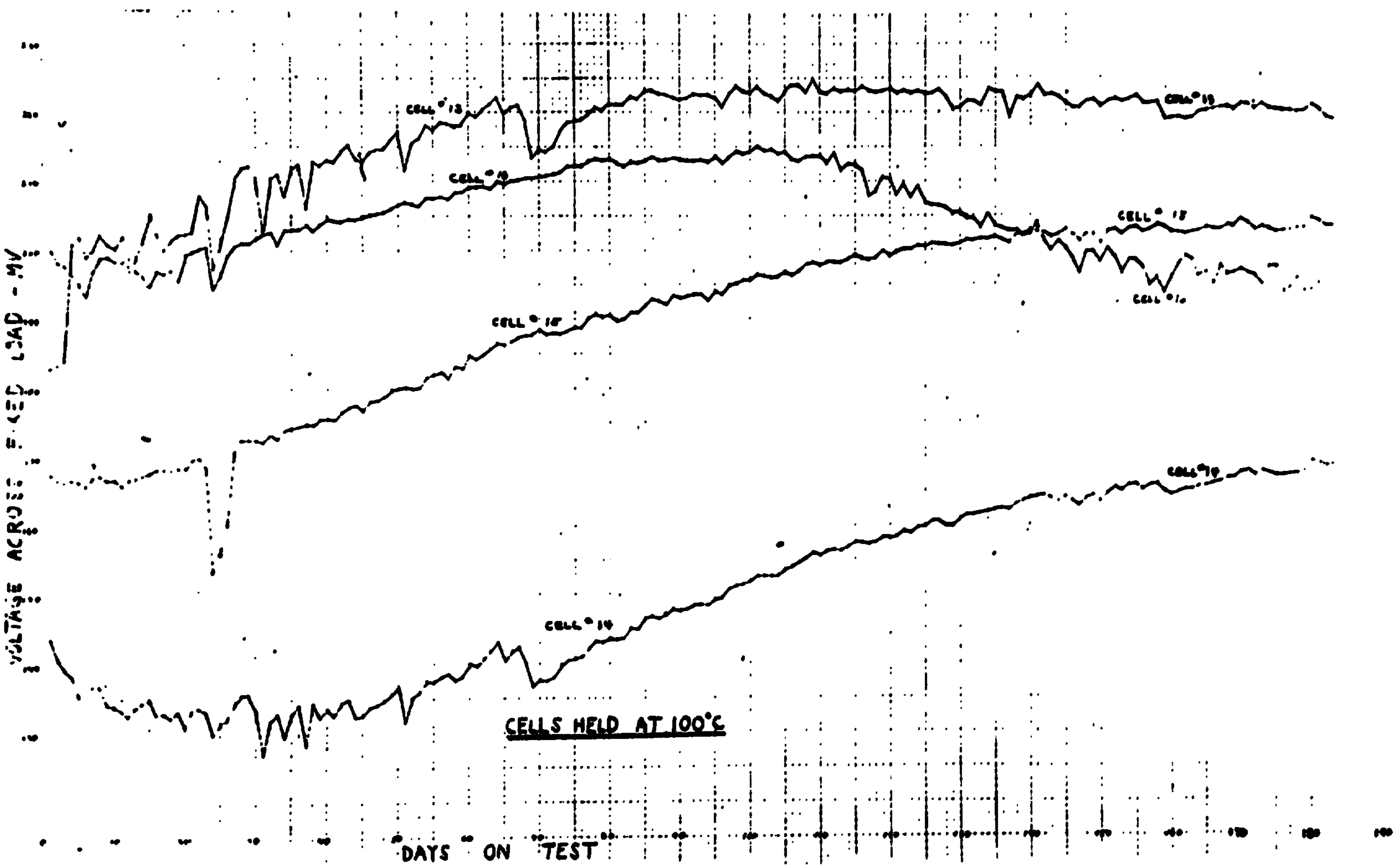
- R_S INCREASING - AT ALL TEMPERATURES
- R_{SH} DECREASING - AT ALL TEMPERATURES
- C DECREASING - AT 100°C ONLY

SOME CORRELATION BETWEEN IN-SITU AND SIMULATOR DATA, BUT MORE ACCURATE IN-SITU DATA NEEDED FOR BETTER CORRELATION.


ROOF TOP EXPOSURE
ENCAPSULATED CdS CELLS
OUTPUT ACROSS FIXED LOAD VS TIME
VOLTAGE ACROSS FIXED LOAD - CORRECTED
DAYS ON TEST
GLASS CRACKED
CELL 1
.36
.34
.32
.30
.28
.26
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
0
60
120
180


CELL #3
CELL #2
CELL #8
CELL #1
CELLS HELD AT 40°C.
DIFFICULTIES WITH TEMPERATURE CONTROL
DIFFICULTIES WITH TEMPERATURE CONTROL
CELL #6
CELL #7
CELL #5
CELLS HELD AT 60°C.
VOLTAGE
DAYS ON TEST


CELL #12
CELL #11
CELL #10
CELL #9
CELLS HELD AT 80°C
DAYS ON TEST


CELLS HELD AT 100°C
DAYS ON TEST

CHANGE IN MAX. POWER - AM1 at 25°C
AFTER SIX MONTHS ACCELERATED EXPOSURE
(Tested by NASA, LEWIS)

Temp. of Exposure	Cell No.	CHANGE IN MAX. POWER
40°C	1	-11.4%
	2	- 0.5
	3	0.0
	4	- 6.3
60°C	5	+ 0.9
	6	+ 0.9
	7	- 1.7
	8	+ 3.6
80°C	9	- 2.3
	10	+ 2.3
	11	+ 0.9
	12	+ 3.1
100°C	13	- 9.9
	14	+ 4.7
	15	+ 9.6
	16	-23.4

SUMMARY
CHANGE IN CELL PARAMETERS
AT AM1-25°C
AFTER SIX MONTHS ACCELERATED EXPOSURE

PARAMETER	Average Percent Change at:			
	40°C	60°C	80°C	100°C
OCV	-0.2	+1.4	+1.6	-1.8
SCC	-1.7	+1.1	+3.4	+12.7
M.P.	-4.6	+0.9	+1.0	-4.8
FILL	-2.8	1.6	-3.8	-14.4
R_S	+65	+54	+49	+134
R_{SH}	-51	-36	-51	-60
C	-2.1	-0.4	-1.3	-35.4

E- SUMMARY OF KEY RESULTS

1. CdS Cell Fabrication Facility Operative
   Reached 5% average AM1 efficiency for std. process
   for terrestrial design cell. All cells over 4%.

2. Method developed for applying vacuum evaporated fine mesh
   grid contact - basically low cost method using aperture
   mask.

3. Protected cells show no degradation of output on
   real time test at 6 months

4- Accelerated test of protected cells indicate no probable
   degradation of output under normal conditions
   for at least several years

5- Accelerated test at elevated temperatures and heavier
   duty cycles is showing changes in basic cell
   parameters - which should lead to more accurate
   projections of cell lifetimes

F- MAJOR PROBLEMS

1. VACUUM EVAPORATED GRIDS APPARENTLY SHORTING CELLS.

2- PRINTED GRIDS TOO HIGH IN RESISTANCE AND TOO COARSE IN RESOLUTION.

G- PLANNED ACTIVITY - NEXT 6 MONTHS

1- UPGRADE STD PROCESS FACILITY FOR
   HIGHER OUTPUT (> 5%), MORE REPRODUCIBLE,
   HIGH YIELDS
   - A- QUALITY & HOMOGENEITY OF CDS FILM
   - B- TOPOLOGY & STRUCTURE OF SUBSTRATE
   - C- DOPING OF Cu_2S LAYER
   - D- OPTIMIZE ETCH & DIP PROCESS

2- CONTINUE DEVELOPMENT OF LOW COST GRID
   - A- EVAPORATED METAL - NON-SHORTING CONTACT
   - B- PRINTED GRID - LOWER RESISTANCE, FINER RESOLUTION
   - C- DEVELOP INTERCONNECTION FOR FINE & COARSE GRIDS

3- DEVELOP ENCAPSULATION - PASSIVATION MEANS
   - A- CONTROL Cu_2S SURFACE STATES - H_2, AR, N_2
   - B- ENCAPSULATION - SiO_2, Al_2O_3, Si_3N_4 EVALUATE FOR IMPERMEABILITY, COMPATIBILITY, OPTICAL COUPLING, LONG LIFE
   - C- EVALUATE MULTIPLE COATINGS - FOR OPTIMIZATION OF CONFLICTING REQUIREMENTS

4- CONTINUE LIFE TESTING
   - A- CORRELATE REAL TIME & ACCELERATED TEST RESULTS
   - B- IDENTIFY MODES OF DEGRADATION
   - C- DETERMINE MAGNITUDES OF EACH & ACTIVATION ENERGY WHERE APPLICABLE
   - D- PROJECT LIFETIMES FOR EACH DEGRADATION MODE FOR TYPICAL EXPOSURES & DUTY CYCLES

G- PLANNED ACTIVITY - NEXT 6 MONTHS

5- STUDY WAYS TO INCREASE CELL OUTPUT

- A- SCC - INCREASE ABSORPTION, IMPROVE LIFETIME IN Cu_2S
- B- OCV - INCREASE BY SELECTED DOPING
- C- FILL FACTOR - DECREASE R_S - INCREASE R_{SH}
- D- ALTERNATE CELL CONSTRUCTIONS
- E- ANALYSIS OF LOSSES IN CELLS

6- REDUCE EVENTUAL COST POTENTIAL

- A- LOWER COST MATERIALS
- B- THINNER LAYERS - PARTICULARLY CdS
- C- IMPROVE PROCESSING

7- STUDY COMPOSITION & STRUCTURE OF Cu_2S/CdS

- A- HIGH VS LOW OUTPUT CELLS
- B- SEM & DIMA STUDIES OF JUNCTION REGION
- C- BASIC STUDIES AT UNIVERSITY OF PITTSBURGH