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N76 12492

DIRECT SOLAR ENERGY CONVERSION

FOR

LARGE SCALE TERRESTRIAL USE

AER 72-03478

Formerly GI-34872

6/1/72 - 6/30/75
$981,000

7/1/75 - 6/30/76
$484,974

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National Solar Photovoltaic Program Review Meeting

July 22-25, 1973
Los Angeles, California

OBJECTIVES

1) Improve cell performance, stability and life expectancy
2) Improve understanding of cell mechanisms with direct experimental verification
3) Improve gridding and encapsulation to improve life expectancy

PAST ACTIVITIES

As a result of the three year program up to June, 1975, major advances have been made in the reproducible production of CdS cells, the understanding of cell formation and operation mechanisms and the understanding and control of cell degradation mechanisms.

Cells can now be reliably made on copper/zinc, molybdenum, Fe-Ni, zinc and cadmium stannate on quartz. In February, 1975, a run of 60 large (55 cm^2) cells produced a yield of 85% with a mean efficiency of 4.4% and a maximum efficiency of 5.2%. During May, 1975, 20 small (4 cm^2) control cells were produced with a mean efficiency of 5.5% and a maximum efficiency of 6.0%. These efficiencies are under Tungsten-Iodine simulation; the cells are blue sensitive and roof-top testing generally shows a 10% enhancement. The best cell to date shows a 6.8% natural insolation efficiency. Cells are generally made on Cu/Zn substrates with a CdS layer of 20-25 micron thickness.

Procedures and controls have been refined to the extent that transfer to other groups and organizations can be successfully accomplished.

The influence of temperature and illumination intensity on Cell I-V characteristics have been used to identify the effective barrier height, to isolate the effects of blocking contacts and to non-destructively determine the stoichiometry of the surface copper sulfide.

A major improvement in reproducibility and cell performance has been achieved by extensive vacuum heat treatments after cell gridding and lamination. Degradation due to interaction with oxygen and water vapor can be reversed by either hydrogen or vacuum heat treatment.

Roof top testing of cells protected from the atmosphere has shown no detectable degradation after twenty months. Accelerated testing has been conducted at temperatures from 46 to 85°C in various ambients. Lifetimes (degradation to 1/e of initial performance) in excess of twenty years have observed at ≤50°C. It is concluded that suitably hermetically sealed cells will be adequately stable for terrestrial applications.

Quantitative descriptions of the short circuit current have been developed and the importance of reflection from the substrate in front wall cells revealed.

The dominance of interface recombination in controlling the open circuit voltage has been identified.

Structural studies have resulted in a more complete understanding of the cell. Minority carrier diffusion distances have been measured in actual cells. Some changes occurring during degradation have been identified.

During the initial part of the program, studies of toxicity problems and economic assessments established that neither of these considerations presented likely obstacles to large scale utilization of CdS Solar Cells.

CURRENT ACTIVITIES

Various techniques to increase the open circuit voltage are being explored. It had been previously observed that cells made on CdS deposited from a single source gave a consistently higher V_{oc}. Further tests have now shown that this effect may in fact relate to differences in source and substrate temperatures. The resulting differences in CdS structure and crystallinity are being documented. Deposits of mixed CdS and ZnS are being produced and will be initially made into cells using the conventional barriering technique. Precision lattice parameter measurements will be used to monitor composition.

Analysis of I-V characteristics at temperatures between 25 and 110°C is being perfected to provide non-destructive analysis of the Cu_2S. Changes due to vacuum heat treatments and exposure to oxygen are also being monitored by the same technique. In a parallel O.N.R. program, detailed spectral response measurements are being made.

Ultra-high vacuum equipment is being readied to conduct controlled reaction experiments between the copper-sulfide layer and atmospheric components, to be followed by vacuum heat treatments. In situ mass spectroscopy will identify species emitted during these experiments.

Direct observation of the Cu_2S layer and the interface with CdS is under way using transmission electron microscopy. Atmosphere related degradation will also be followed by this technique.

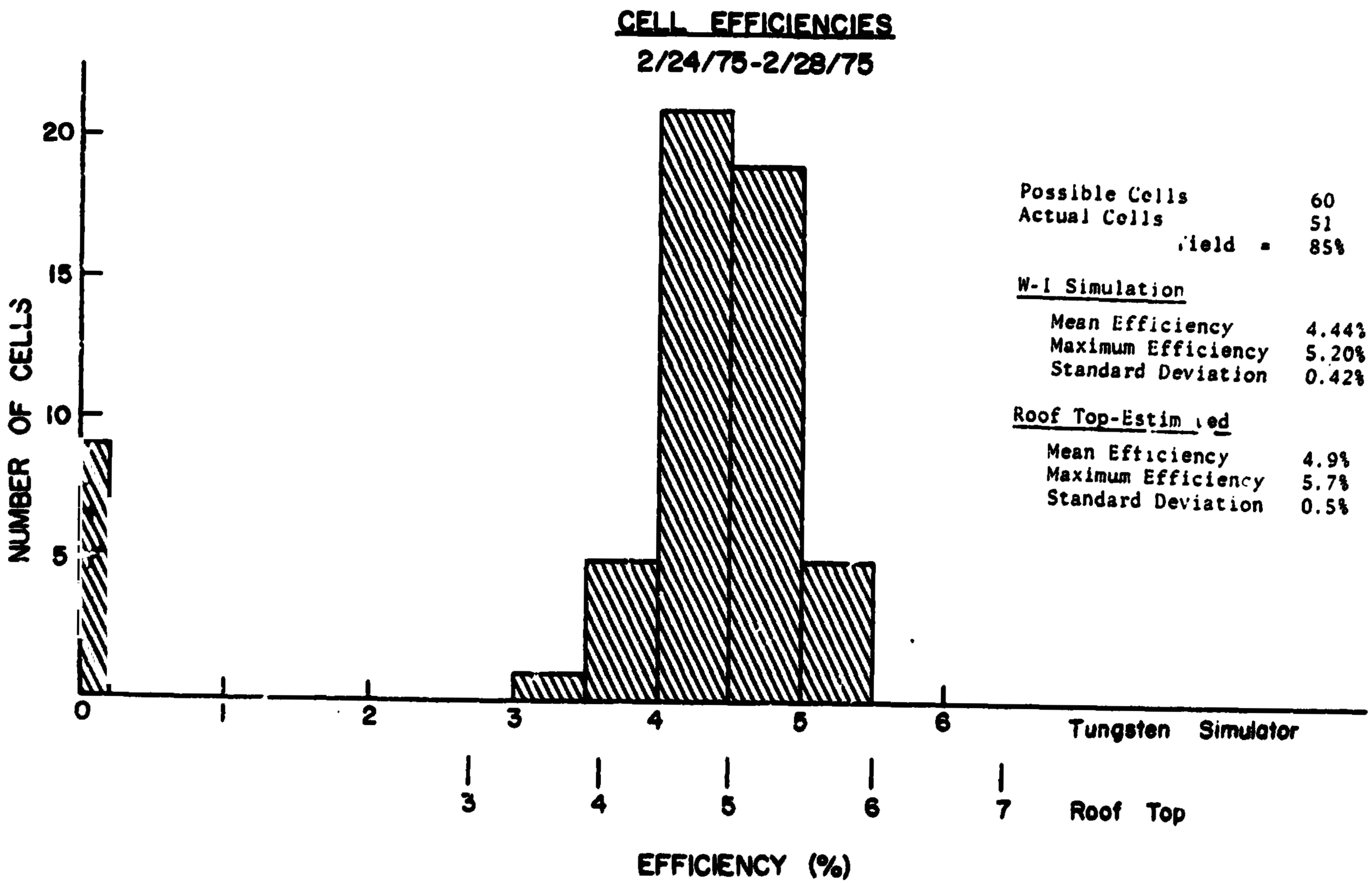
FUTURE PLANS

Primary thrusts during the next 6 months will be directed towards achieving higher open circuit voltages and the fundamental understanding of degradation mechanisms. Techniques to be attempted to achieve the former will include the use of ZnS-CdS mixtures to give a better lattice and electron affinity match to Cu_2S, also the effects of changes in the orientation of the CdS will be explored.

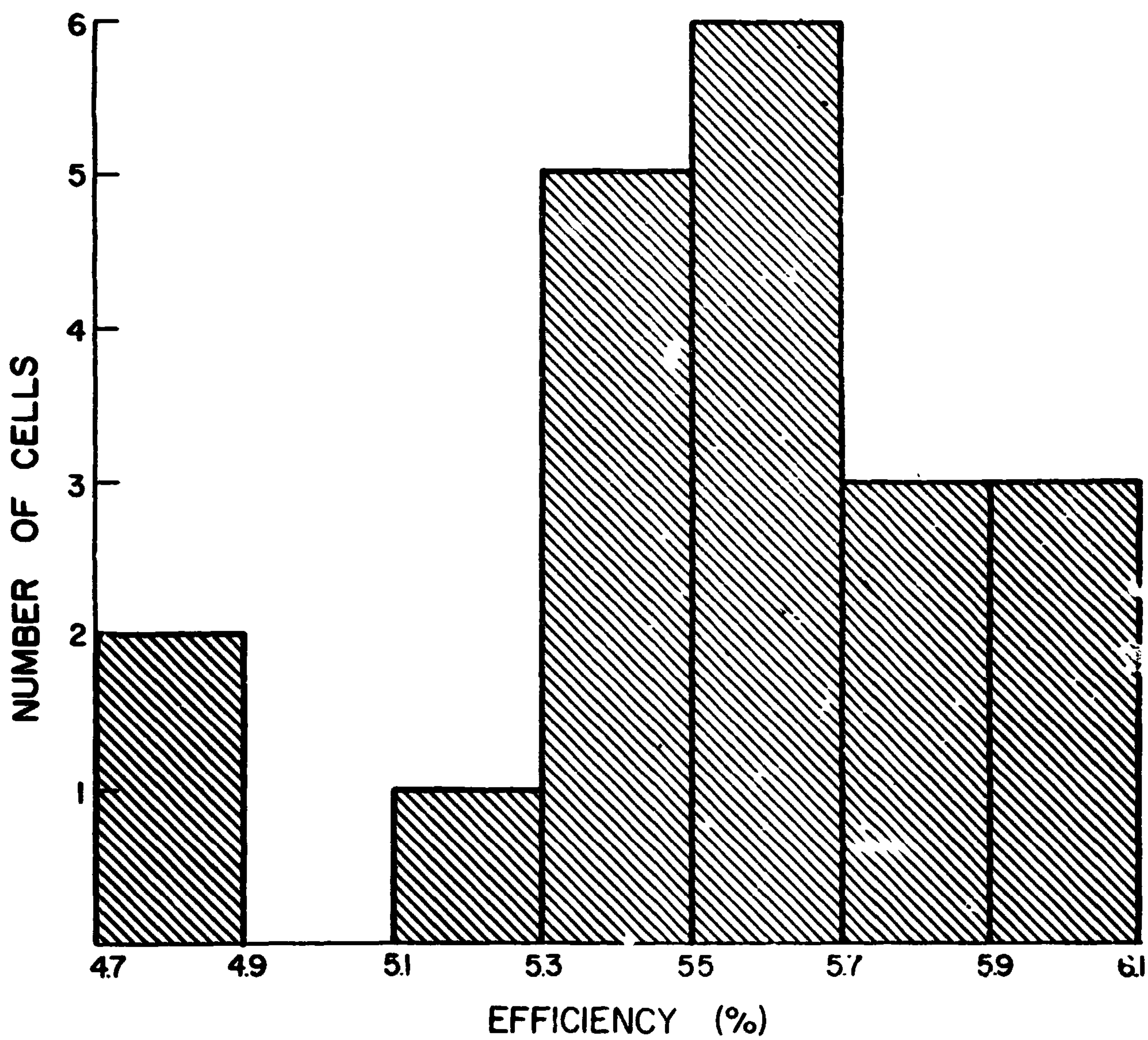
Both theoretical and experimental studies will be made to identify more critically the changes occurring during vacuum heat treatments and exposure to the atmosphere. Support studies of the influence of doping on copper diffusion in CdS, the properties of isolated Cu_2S films and changes in minority carrier diffusion in Cu_2S in various cells are expected to yield valuable results.

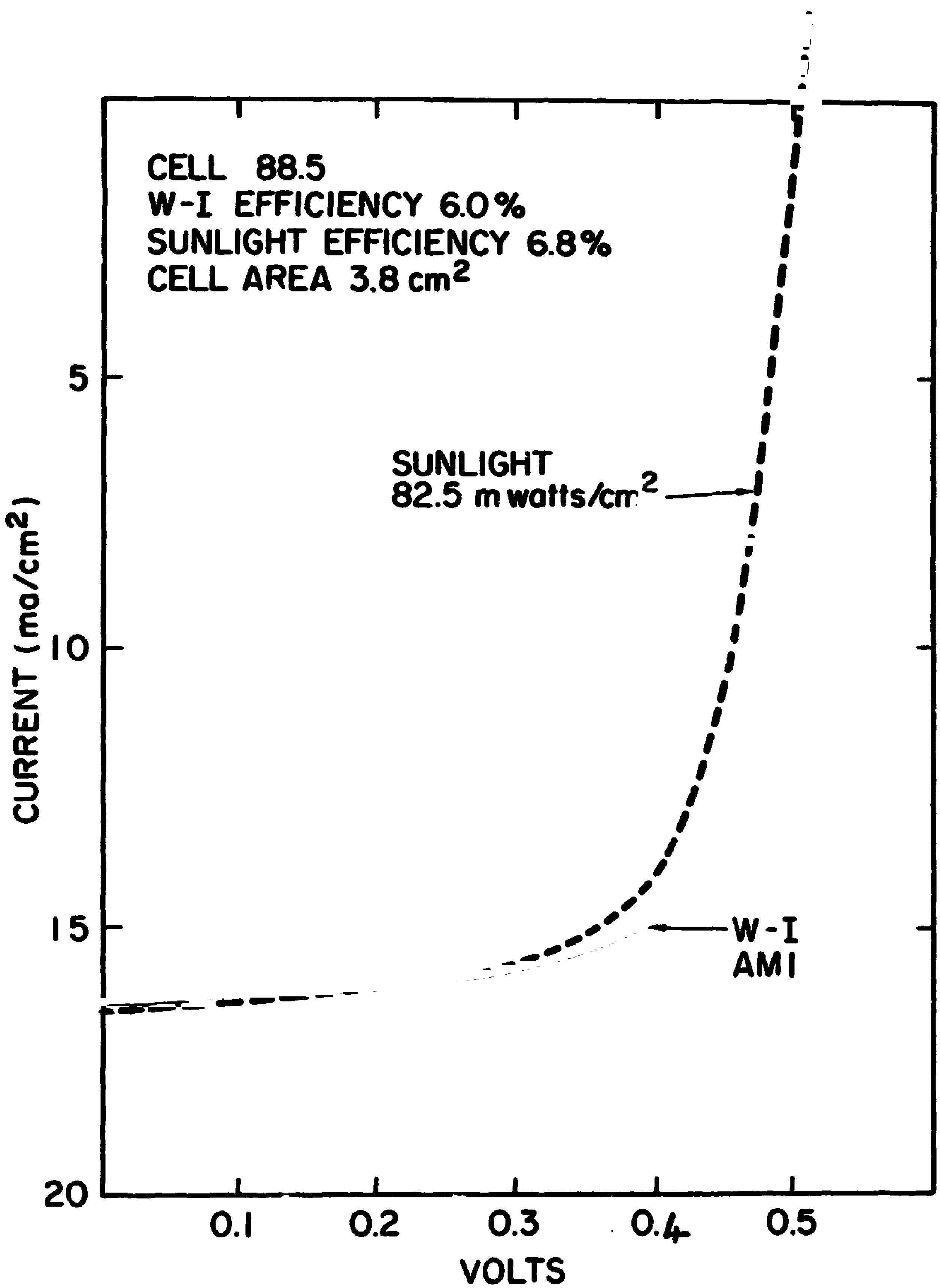
KEY RESULTS

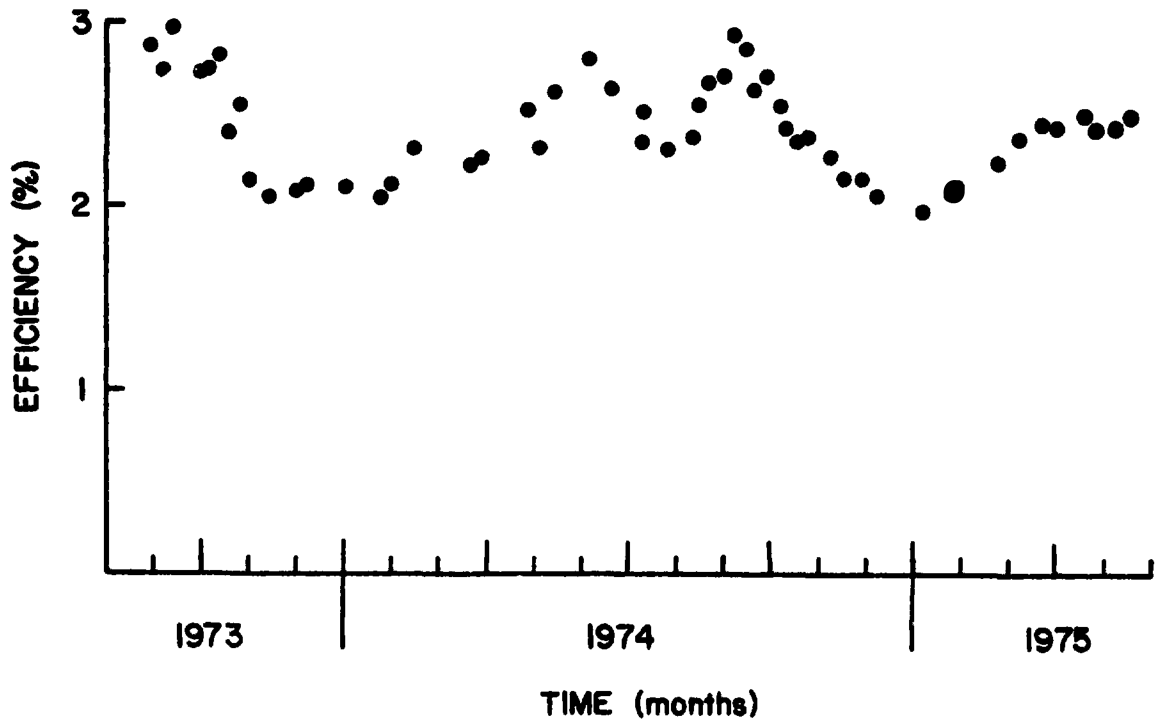
- Reliable production technique developed on low cost metallic substrate.
  Large cells (55 cm^2) of mean efficiency ~5%
  Small cells (4 cm^2) of mean efficiency ~6%
  Best cell 6.8%
- Usable cell life in excess of 20 years supported by roof-top and accelerated testing
- Quantitative description of short circuit current Role of CdS, Cu_2S and the interface region elucidated.
- Dominant role of interface recombination on V_{oc} established. (Conventional model)
- Structure of as-formed cell and effects of degradation substantially established.
- Regeneration accomplished by vacuum and hydrogen heat treatment.


CELL EFFICIENCIES
2/24/75-2/28/75
NUMBER OF CELLS
20
15
10
5
0
1
2
3
4
5
6
Tungsten Simulator
3
4
5
6
7
Roof Top
EFFICIENCY (%)
Possible Cells 60
Actual Cells 51
Yield = 85%
W-I Simulation
Mean Efficiency 4.44%
Maximum Efficiency 5.20%
Standard Deviation 0.42%
Roof Top-Estimated
Mean Efficiency 4.9%
Maximum Efficiency 5.7%
Standard Deviation 0.5%

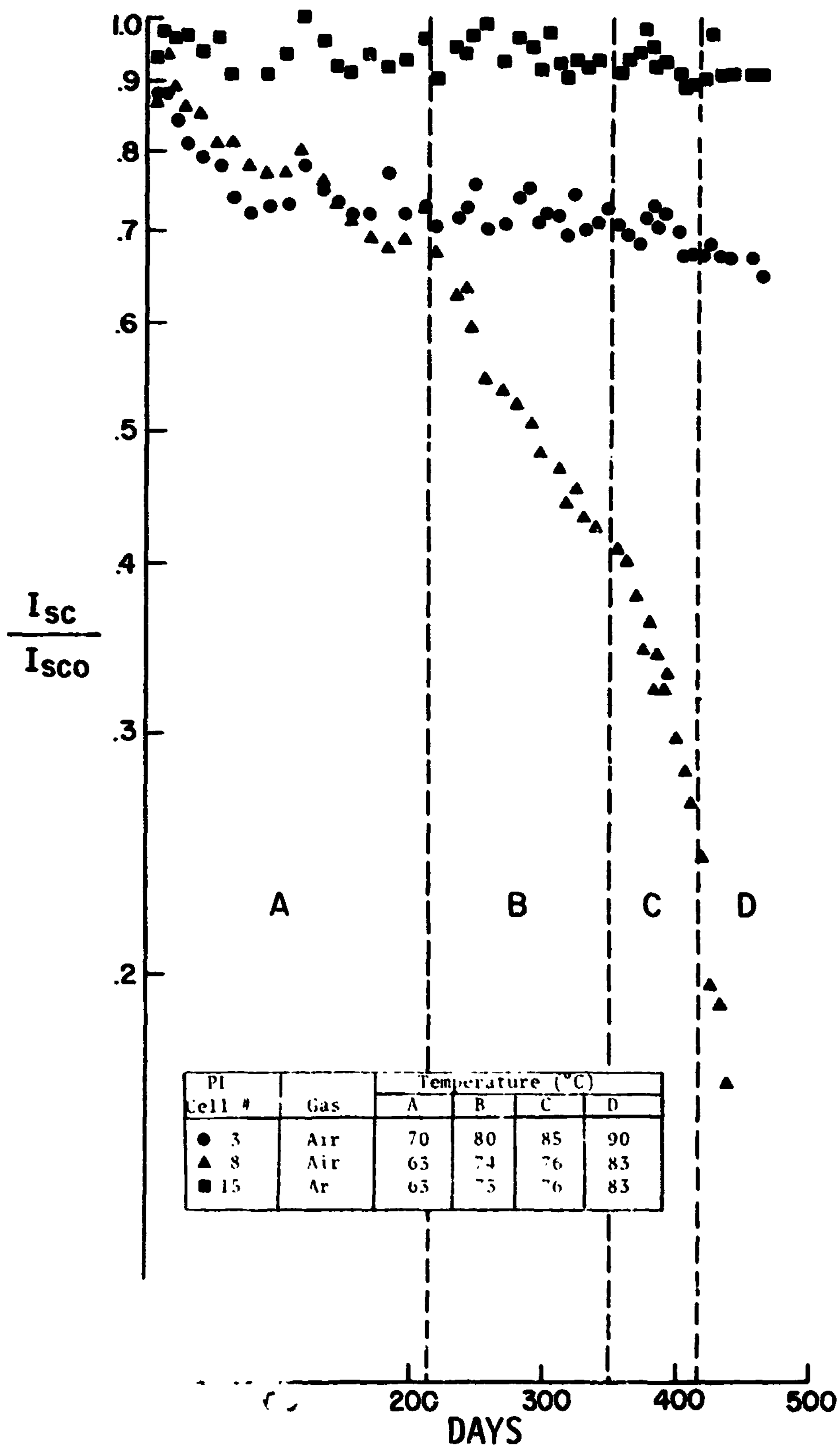
Yield of 4 cm^2 Cells From 5 Copper Substrates
Processed 5/19/75 to 5/29/75.
(Measured on Pilot Line Tungsten - Iodine Simulator)
Average Efficiency = 5.50 % (20 Cells)

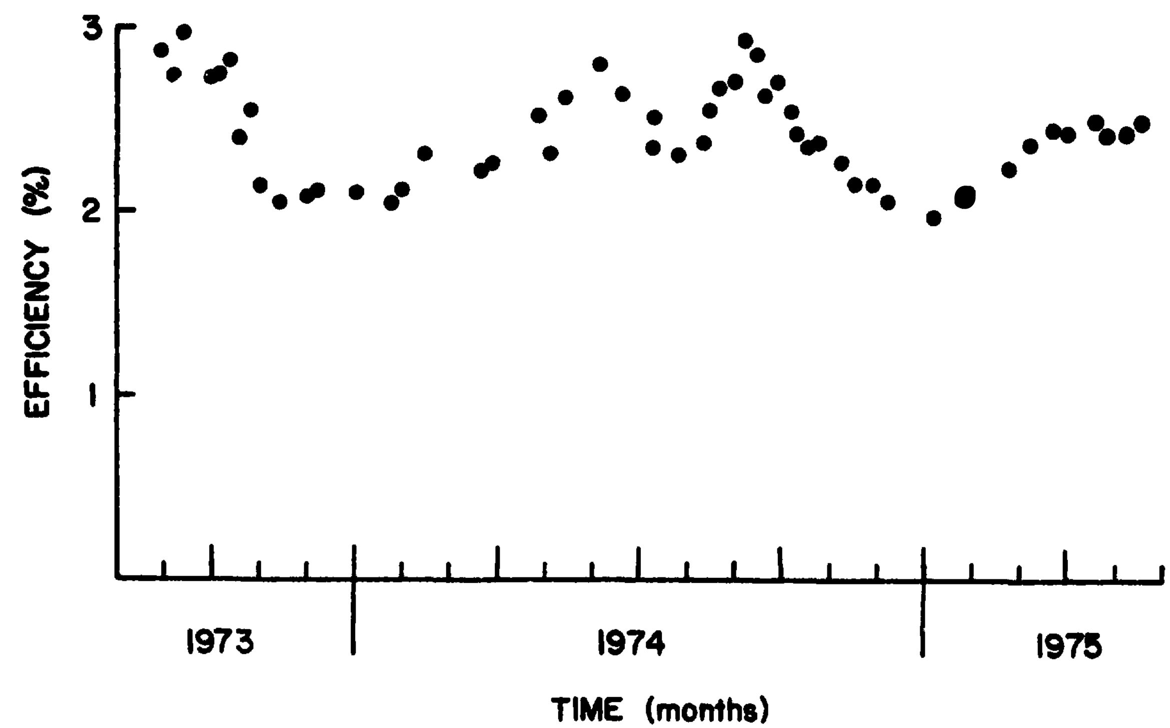



CELL 88.5
W-I EFFICIENCY 6.0%
SUNLIGHT EFFICIENCY 6.8%
CELL AREA 3.8 cm2
SUNLIGHT
82.5 m watts/cm2
W-I
AM1
CURRENT (ma/cm2)
5
10
15
20
0.1
0.2
0.3
0.4
0.5
VOLTS

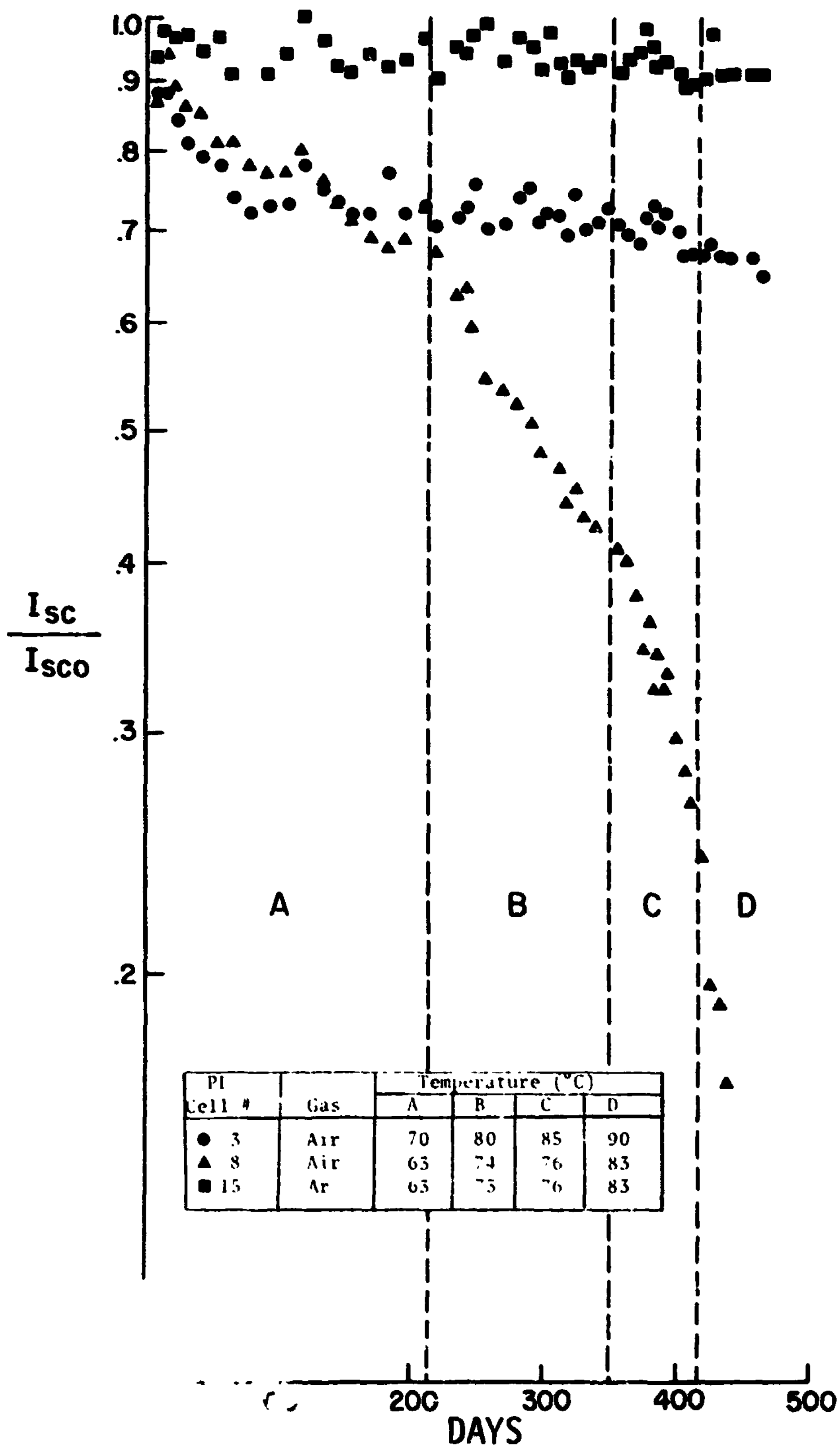


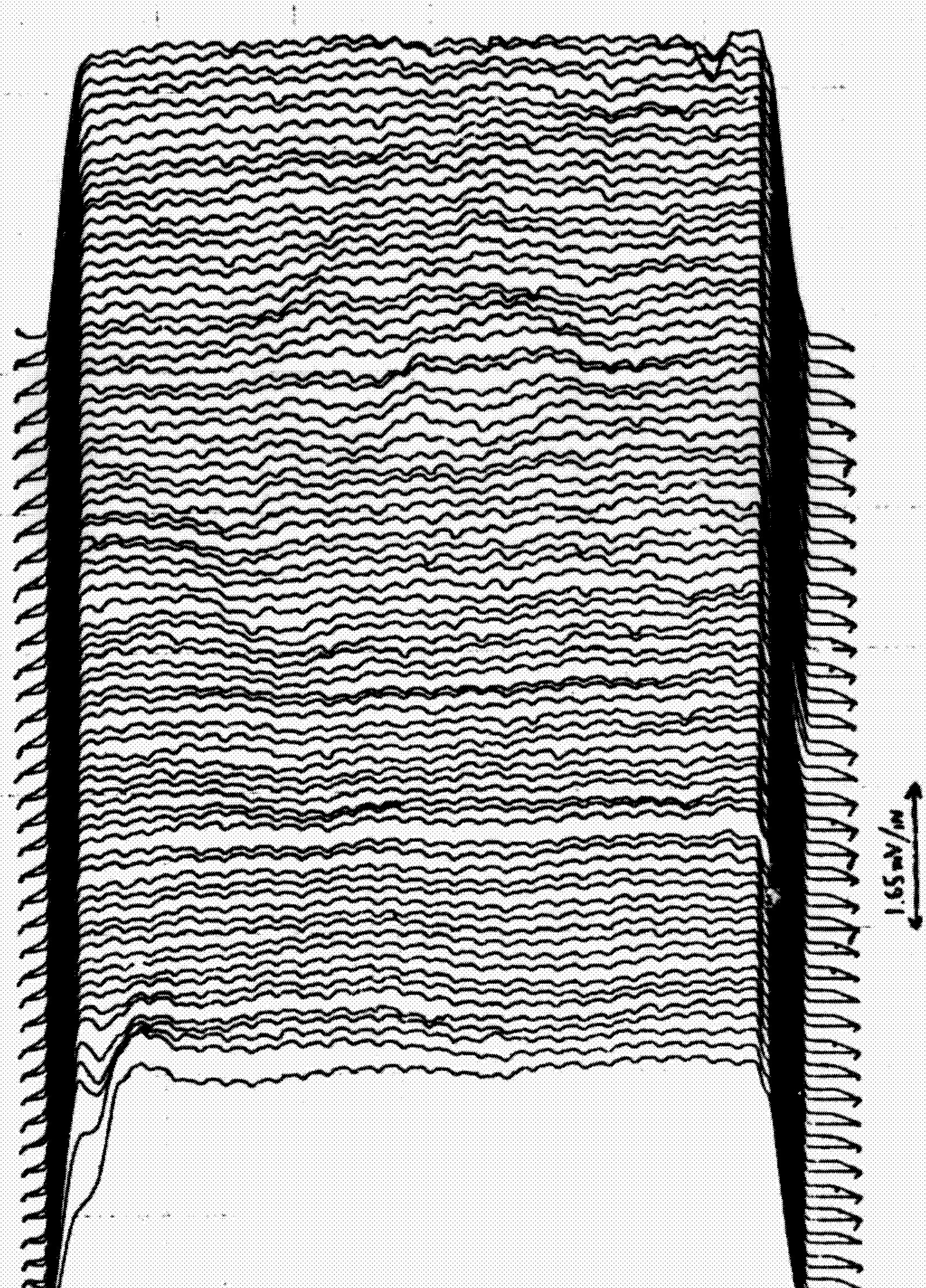
Net ar[illegible] efficiency of 104 cells deployed on Solar One


1.0
.9
.8
.7
.6
.5
.4
Isc / Isco
.3
.2
A
B
C
D
PI Cell #
Gas
Temperature (°C)
A B C D
● 3 Air 70 80 85 90
▲ 8 Air 63 74 76 83
■ 15 Ar 63 75 76 83
200
300
400
500
DAYS



Net ar[illegible] efficiency of 104 cells deployed on Solar One


1.0
.9
.8
.7
.6
.5
.4
.3
.2
Isc / Isco
A
B
C
D
200
300
400
500
DAYS
PI Cell #
Gas
Temperature (°C)
A B C D
3 Air 70 80 85 90
8 Air 63 74 76 83
15 Ar 63 75 76 83



Creeping spot scan of a 3" X 3", 4.3% efficiency cell (#272A2). The short circuit current is plotted as a function of the x-y position of a 4 mm spot.

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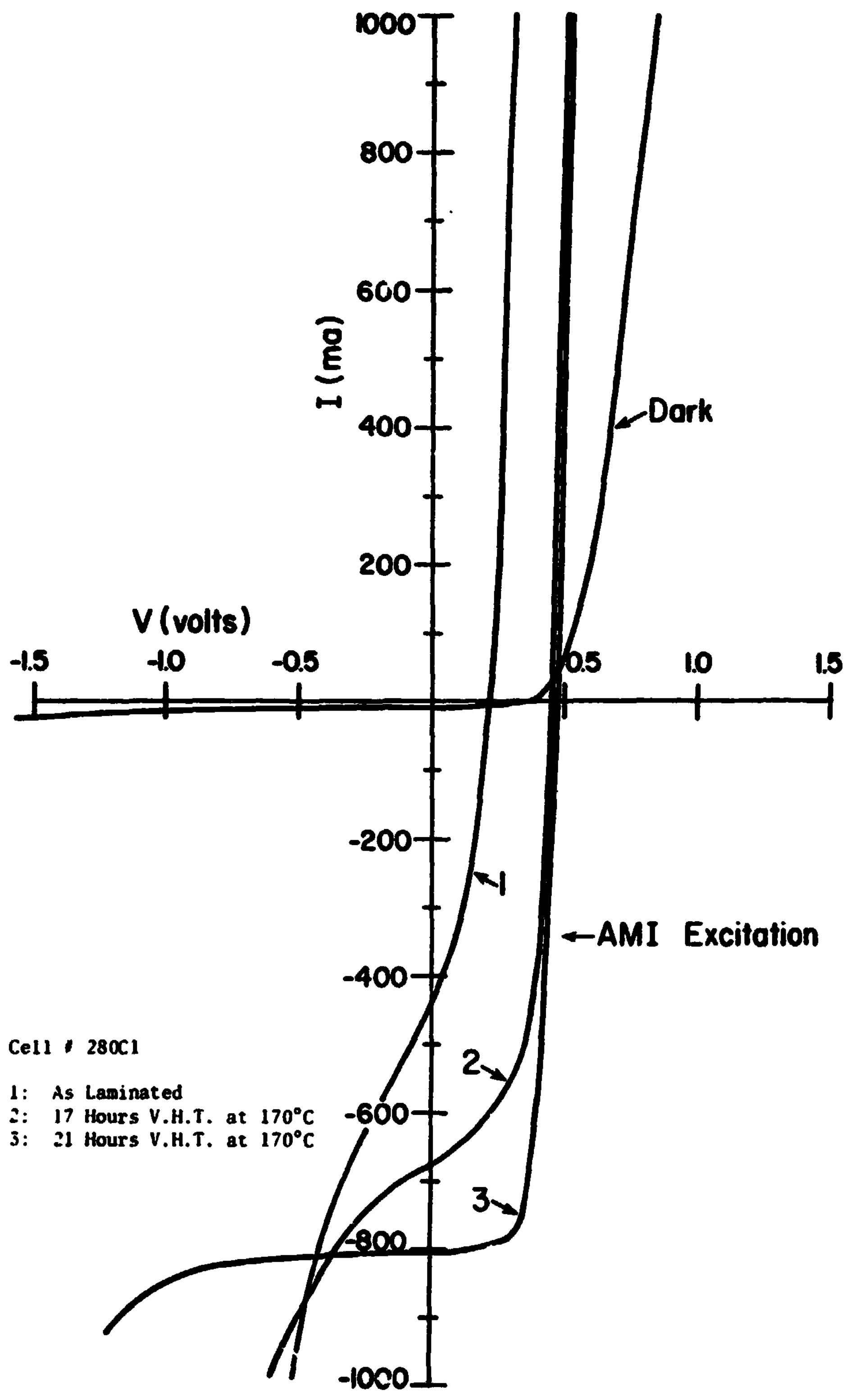
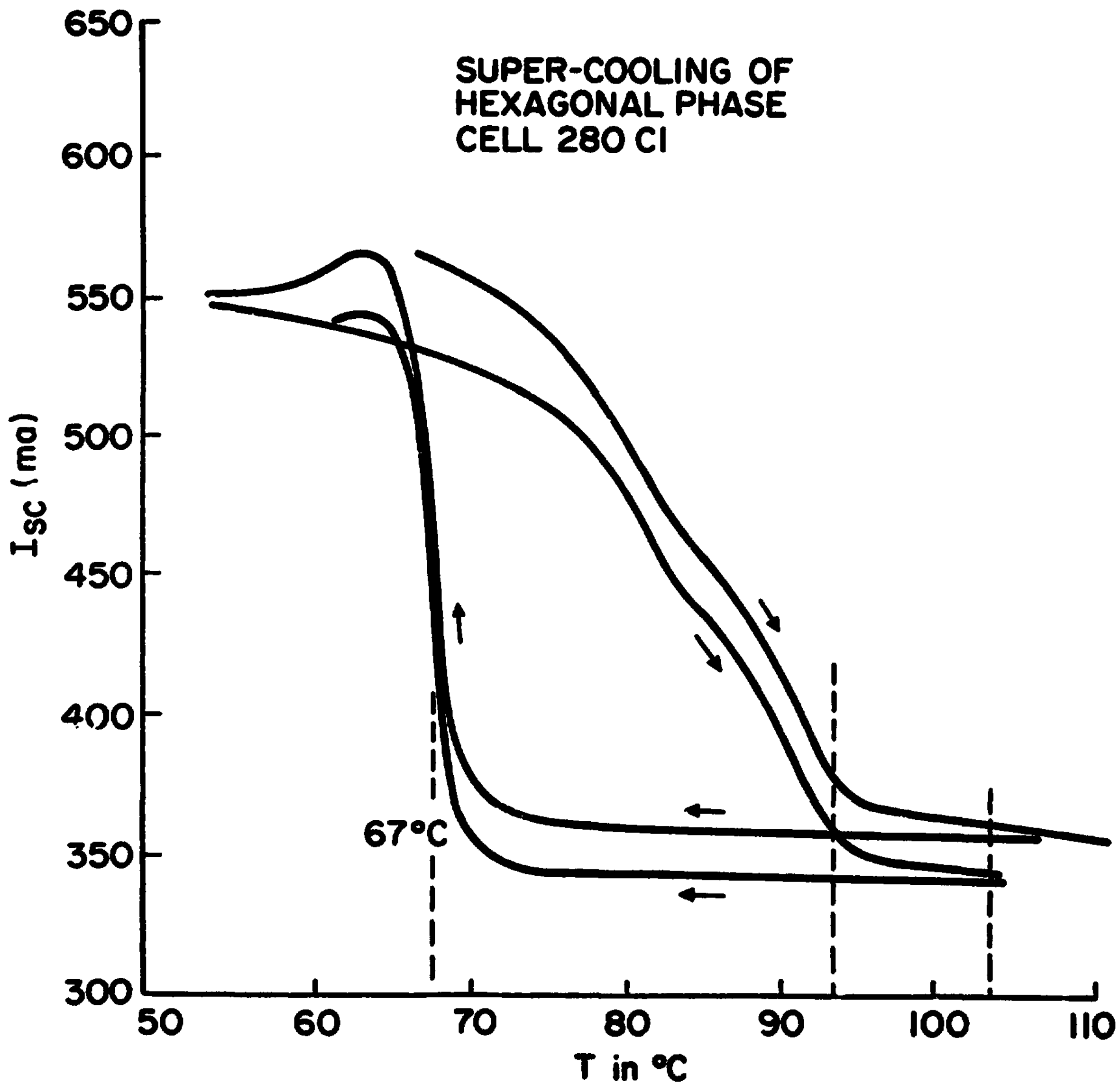
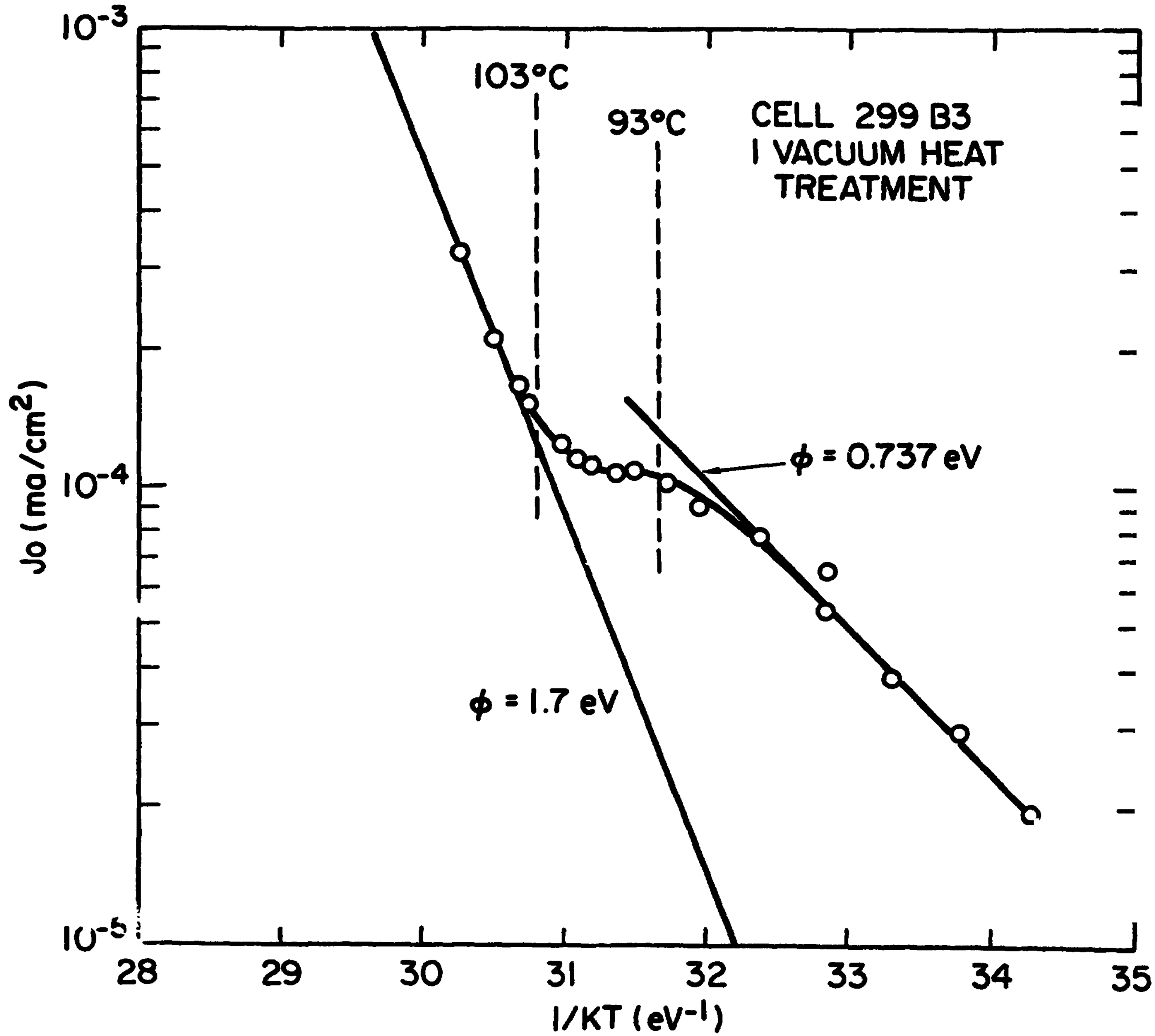
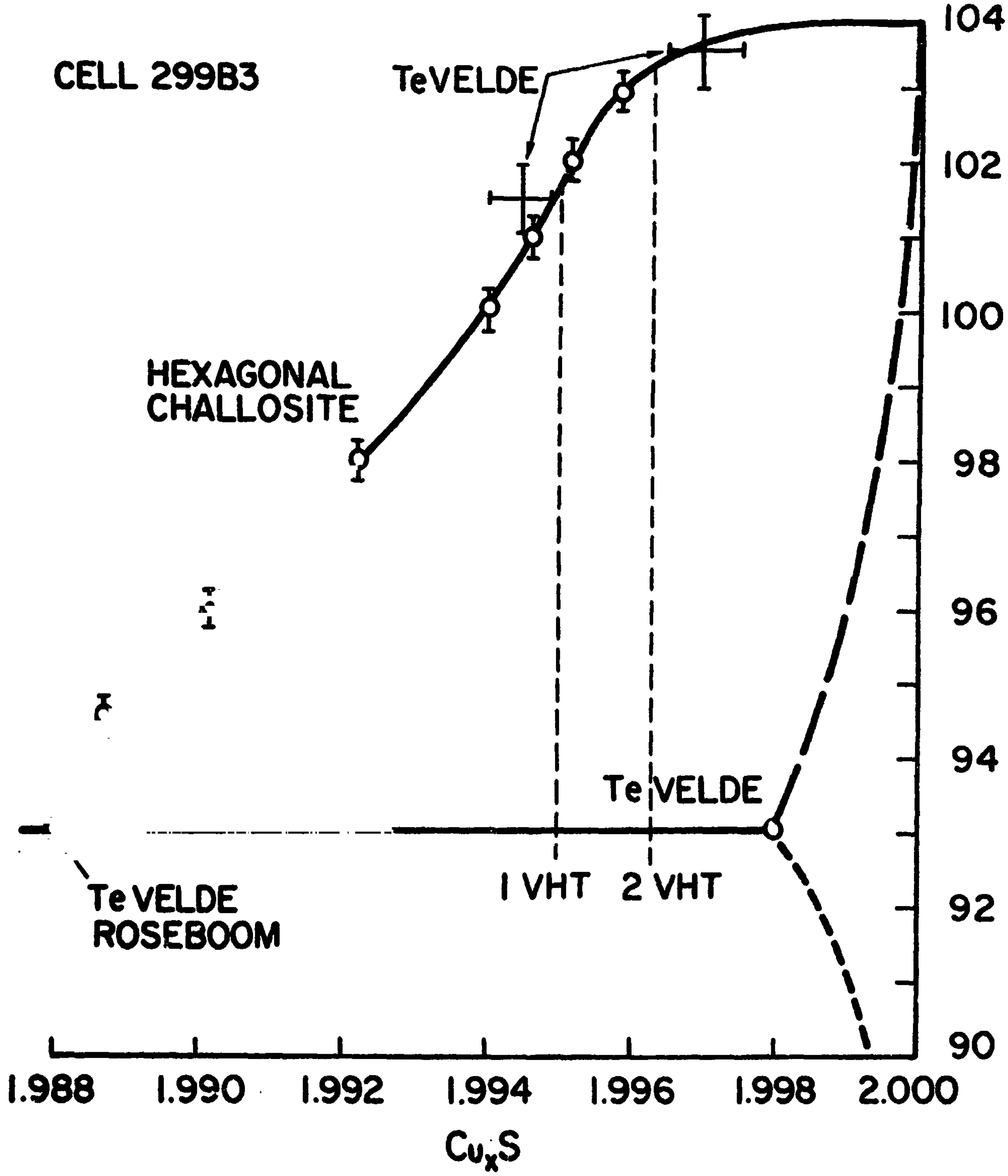
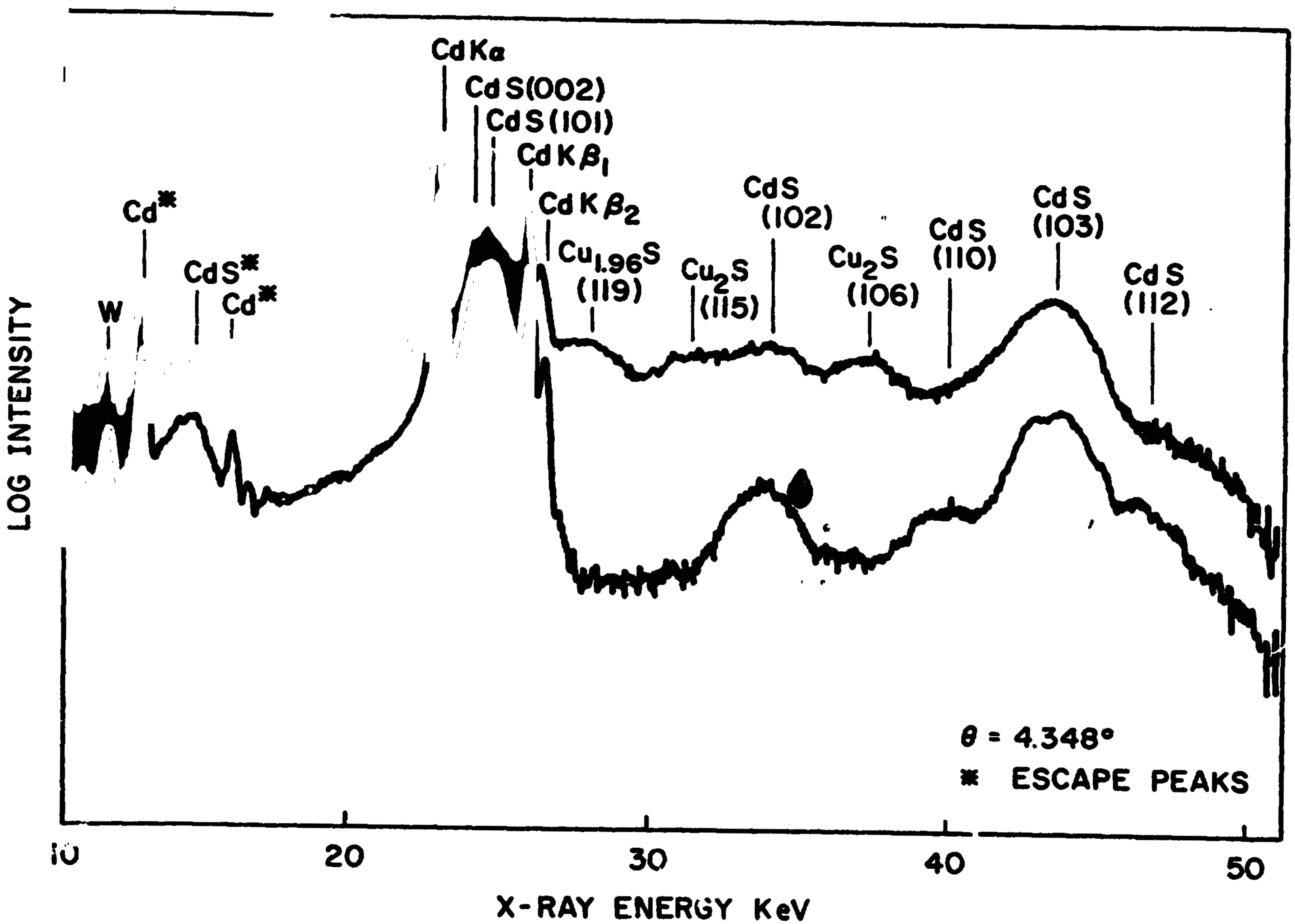

1000
800
600
400
200
-200
-400
-600
-800
-1000
I (ma)
V (volts)
-1.5
-1.0
-0.5
0.5
1.0
1.5
Dark
AMI Excitation
1
2
3
Cell # 280C1
1: As Laminated
2: 17 Hours V.H.T. at 170°C
3: 21 Hours V.H.T. at 170°C


SUPER-COOLING OF
HEXAGONAL PHASE
CELL 280 CI
I_{SC} (ma)
650
600
550
500
450
400
350
300
50
60
70
80
90
100
110
T in °C
67°C


CELL 299 B3
1 VACUUM HEAT
TREATMENT
103°C
93°C
φ = 0.737 eV
φ = 1.7 eV
Jo (ma/cm2)
1/KT (eV-1)
10-3
10-4
10-5
28
29
30
31
32
33
34
35



Influence of vacuum heat treatment on the mean composition of Cu-S phase. The hexagonal chalcocite phase boundary is deduced from the temperature variation of j_0.



Energy dispersive x-ray scan of a Cu_xS layer. Chalcocite (Cu_2S) and djurleite ($Cu_{1.96}S$) peaks are identified in the top curve. The lower curve resulted after the Cu_xS layer was removed by KCN.

455

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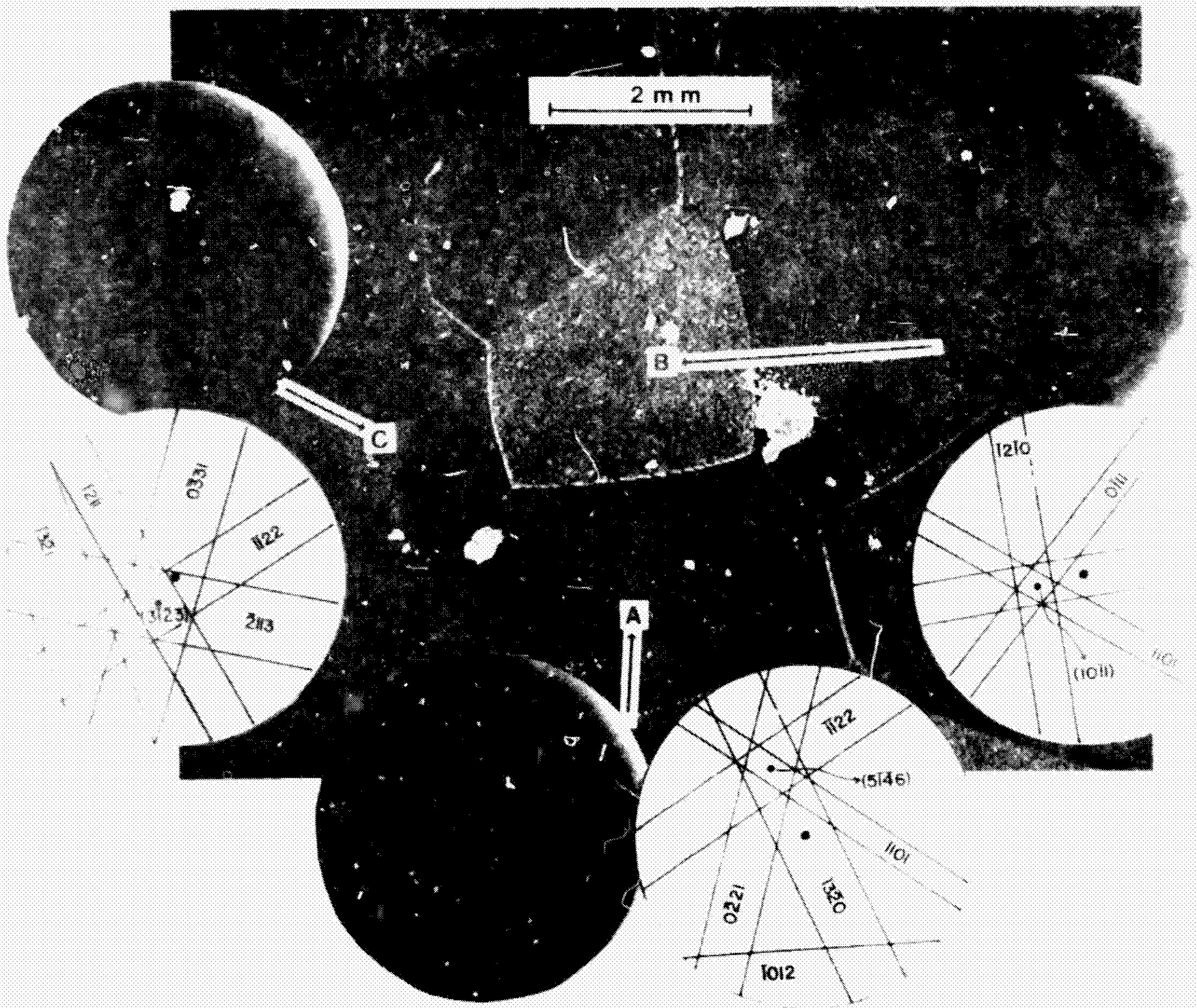
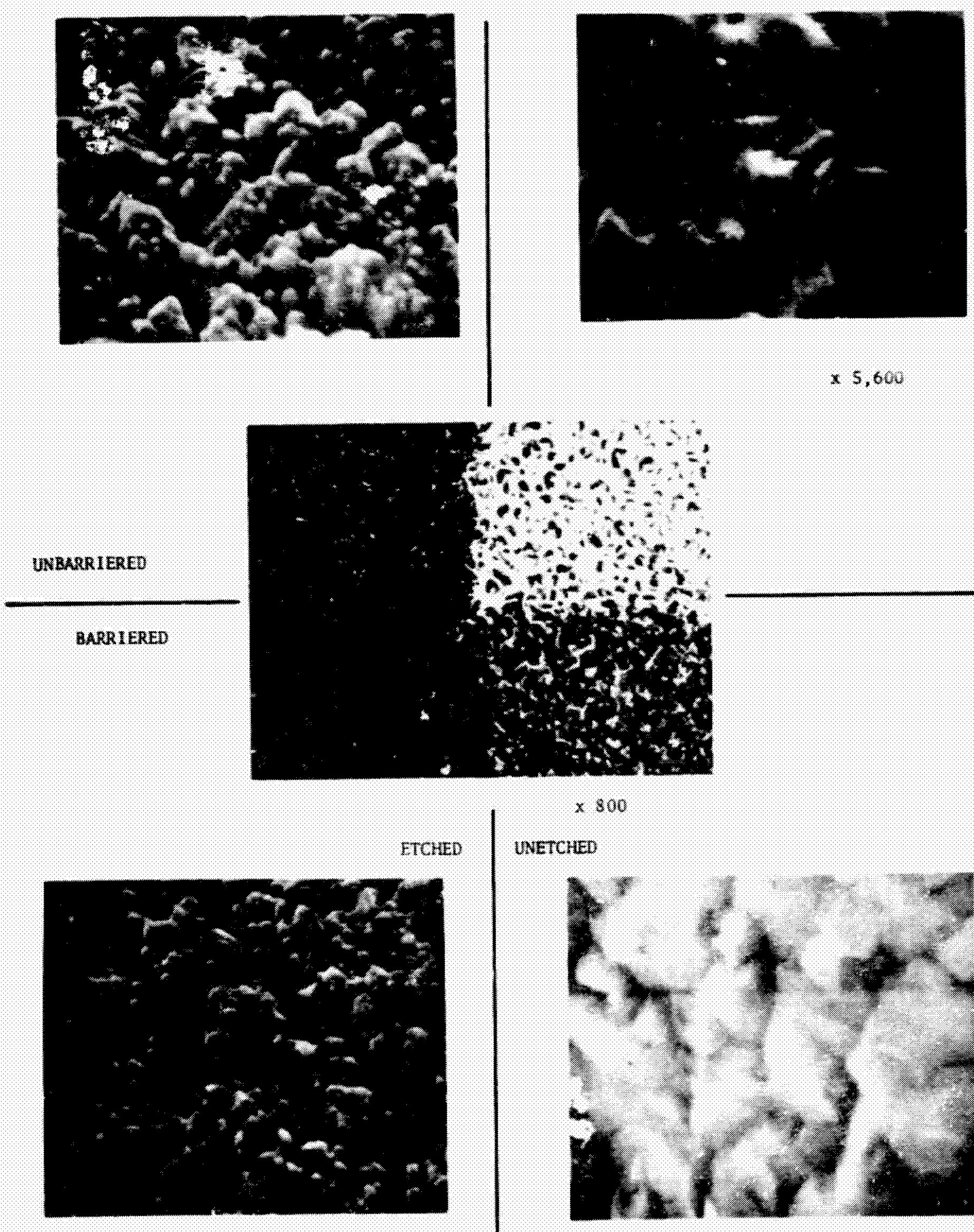
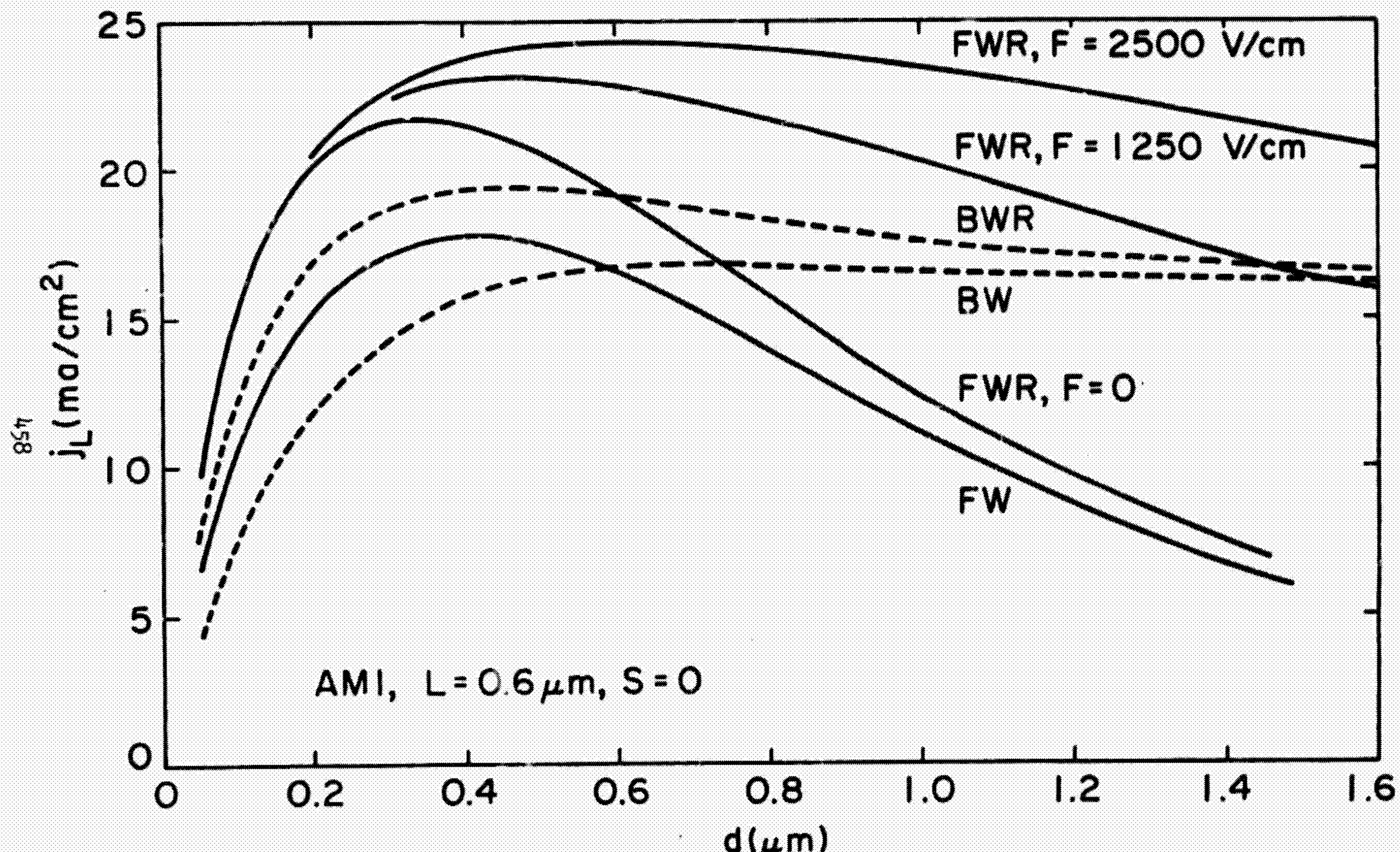


Fig. SEM Micrograph obtained from a vapor-grown CdS film. The insets are channelling patterns from their corresponding grains.

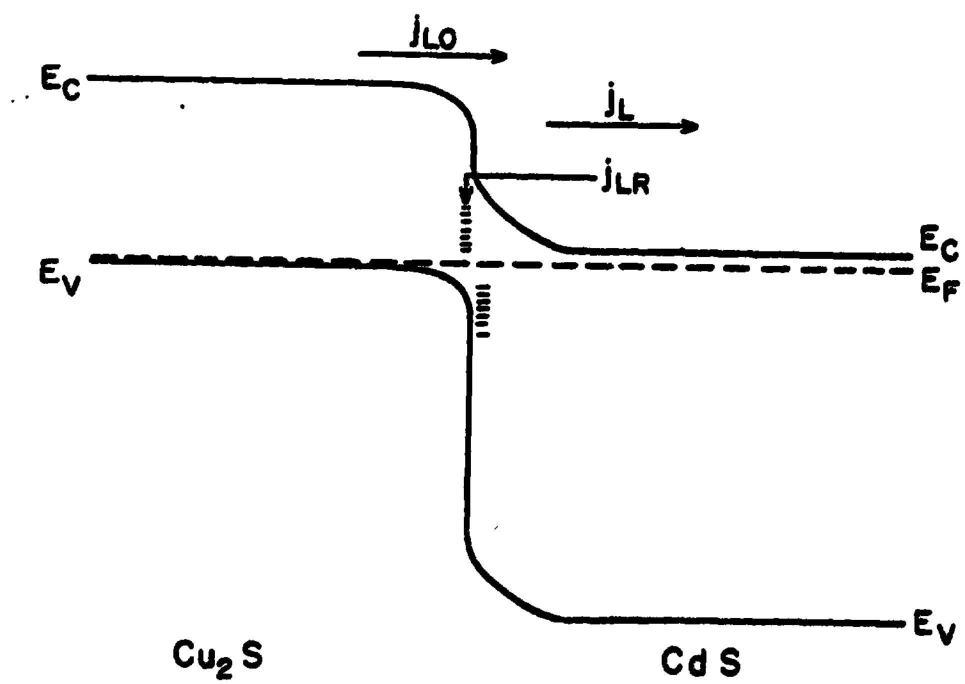
CELL 63-E



C. 6



Calculated current densities, including reflection losses for CdS/Cu_2S cells.
FW - front wall; BW - back wall; R - with reflection. F - field in CdS.
F=0 unless specified.



Band diagram for cell showing junction recombination current j_{LR}

INTERFACE DOMINATED CASE

$$j(V) = qS_I\, N_{c2} \exp[-(qV_D + \delta)/kT] \exp(qV/kT) - j_L(V); \quad V \geq 0.3 \text{ volt}$$

$$j_L(V) = j_{LOO}\, [1 - (\frac{d}{R})\, (1 - \frac{d}{3R})] \cdot \frac{\mu_2 F_2\, [V, \phi\,(\lambda)]}{S_I + \mu_2 F_2 [V, \phi\,(\lambda)]}$$

$$V_{oc} = V_D + \delta/q + kT/q\, \ln(j_L(V)/qS_I\, N_{c2})$$

Present Diode Parameters

$S_I \simeq 10^6$ cm/sec ;

$S_I = v_{th} \cdot \sigma_n \cdot N_I$

Lattice mismatch, $N_I \simeq 5.10^{13}$ cm^{-2}

$10^{-15} < \sigma_n < 10^{-14}$ cm^2

$v_{th} \simeq 10^7$ cm/sec

At 25°C

$$V_{oc} = 0.9 - 0.49 + 0.025 \ln j_L(V)$$

$j_L = 10$ ma/cm^2 $\quad V_{oc} = 0.468$ V

$j_L = 20$ ma/cm^2 $\quad V_{oc} = 0.485$ V

Ideal case $S_I = 0$

$$j(V) = qN_{c2}\, L/\tau_n \exp(-E_{q1}/kT) \exp(qV/kT) - j_L; \quad V \geq 0.3 \text{ volt}$$

$$j_L = j_{LOO}\, [1 - (\frac{d}{R})\, (1 - \frac{d}{3R})]; \quad L/\tau_n \simeq 5.10^4 \text{ cm/sec}$$

Thus $V_{oc} = 1.2 - 0.42 + 0.025 \ln j_L(V)$

at j_L = 20 ma/cm^2 $\quad$ V_{oc} = 0.86 volts