N76 12495

INVESTIGATION OF THIN FILM SOLAR CELLS BASED ON Cu_2S AND TERNARY COMPOUNDS SUCH AS $CuInS_2$

BROWN UNIVERSITY

Principal investigator: J.J. Loferski

Talk presented by: J. Shewchun

NSF/RANN GRANT GI-38102X

1 July 1973 to 30 June 1976

~ $100,000/annum.

Abstract

The work at Brown University is concerned with the production and characterization in film form of Cu_2S and related Cu compounds such as $CuInS_2$ for photovoltaic cells. The low cost process technology being examined,namely the sulfurisation method , is capable of producing films on various substrates. Cathodoluminescence is being used as a diagnostic tool (in conjunction with other aids such as x-rays, scanning electron microscopy, etc.) to identify Cu_xS and $CuInS_2$ compounds. Also, single crystals of $CuInS_2$ are being prepared and it is contemplated that p-n junctions will be made in such crystals.

Cu_2S films have been prepared on silicon, cadmium sulfide, aluminum and silica. X-ray analysis is used to identify the particular phase produced. A film of at least 9000A° of Cu_xS is needed to make a positive identification, although films as thin as 4500A° have been identified. We have been able to employ cathodoluminescence for phase identification below these limits with a minimum detectable limit, at present, of about 1500A° of Cu_2S. Scanning electron microscopy is being employed to determine structural features and homogeneity. The films appear to consist of hexagonal platelets whose size depends on film thickness (1500A° of Cu yields crystallites of ½ μm diameter; 9000A° of Cu yields crystallites of 2 μm diameter). Thinner films show orientation effects which give rise to a characteristic x-ray pattern which we have previously designated UA.

Cathodoluminescence measurements have been further refined. Only Cu_2S of all the phases gives a luminescence response and the response is at

9660A° (77°K) with a half width of about 200A°. This is more characteristic of a direct transition behaviour in contradiction with what is generally assumed about Cu_2S. Cathodoluminescence has also been carried out on heat treated (200°C in air for 5-30 min) and copper treated (60A° Cu, 200°C in air for 10-30 min) films. Short-circuit current increases by factors of about 8 (heat treated)to 17 (copper treated) have been observed. Corresponding to this, cathodoluminescence reveals some interesting behaviour. For heat treated films the Cu_2S peak is retained but there is a strong background due to either Cu impurities or defects. For Cu treated films, the Cu_2S peak disappears. In the case of Cu treated films, x-rays reveal that Cu_2S is still present but other unidentified lines are also present.

Diodes formed on single crystal CdS have reasonable I-V characteristics with $V_{OC} \sim 0.45 - 0.5$ volts. Although method efficiencies have only been about 1% (AM1), no optimization of the process has been carried out.

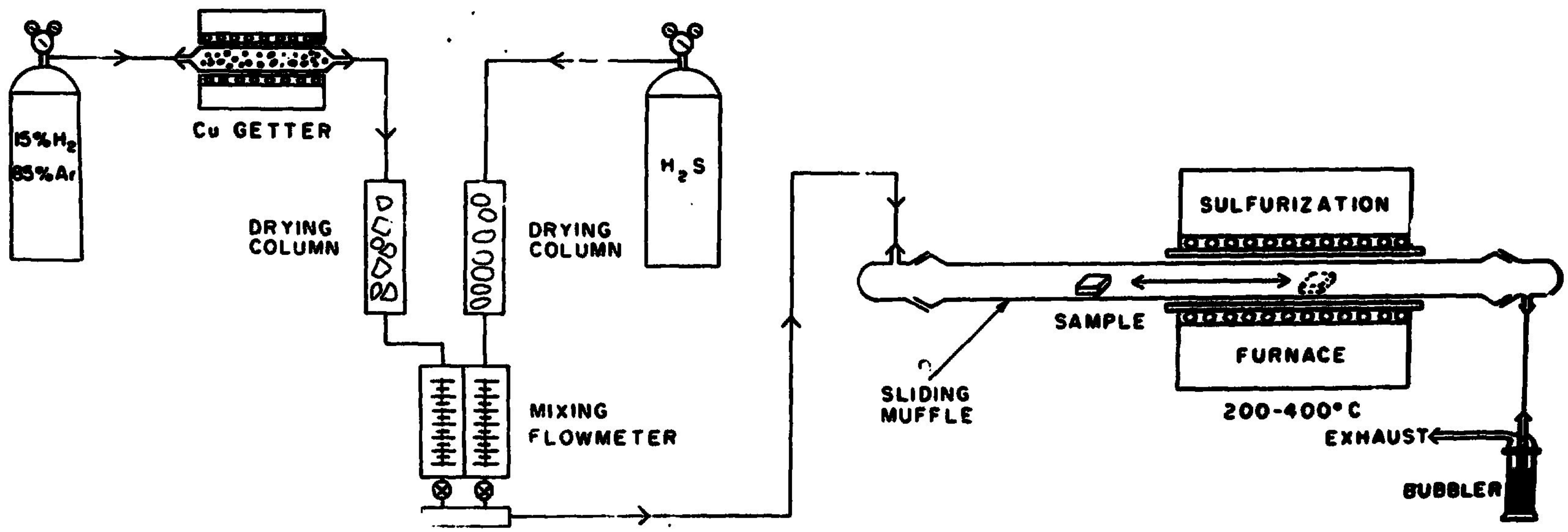
During the next six months we plan to optimize the process for sulfurization of Cu on single crystal CdS with the objective of cell efficiencies of $\sim$ 5%. We plan to construct all thin film cells consisting of (a) Cu sulfurized on quartz or metal substrates followed by (b) deposition of a suitable semiconductor - CdS or a more optimum mate. Cathodoluminescence diagnostics will be refined since they appear capable of identifying the phase of Cu_xS responsible for the strong photovoltaic effect. In addition we plan to expand our activity on the growth of $CuInS_2$ crystals and preparation of p-n junctions.

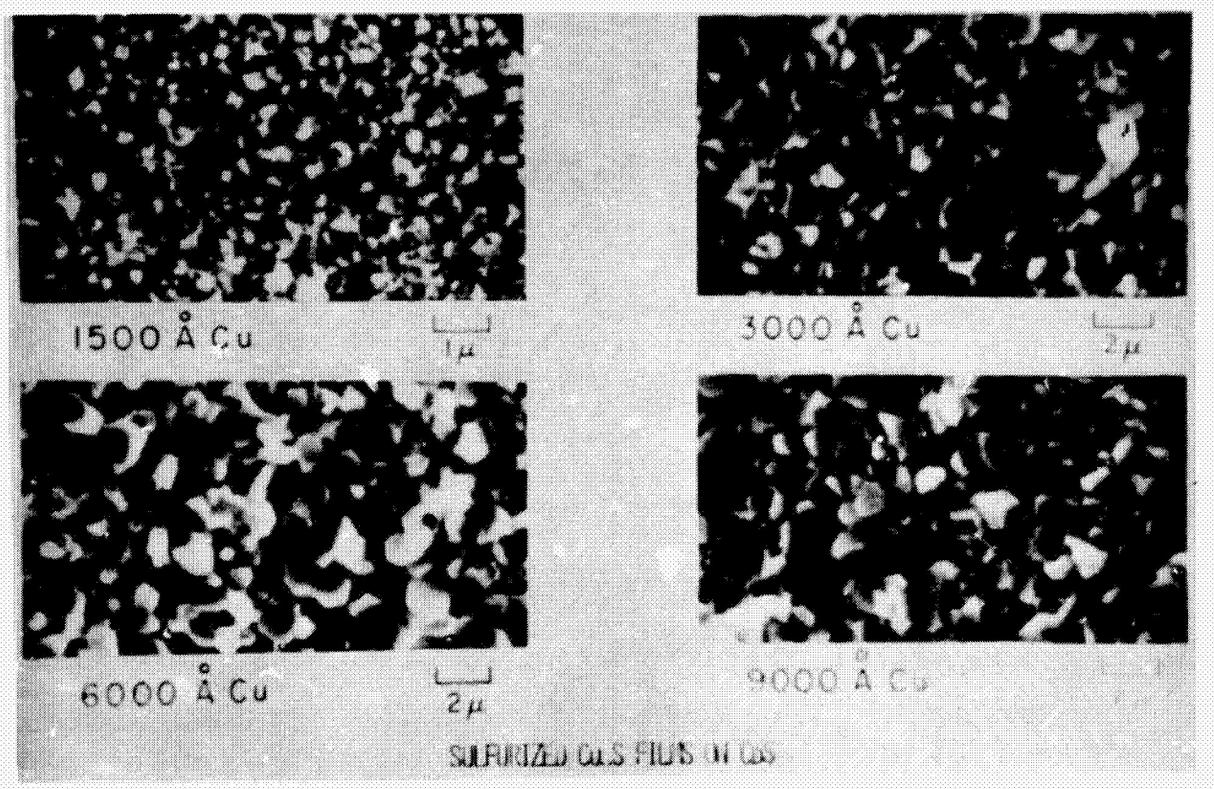
Program Objectives

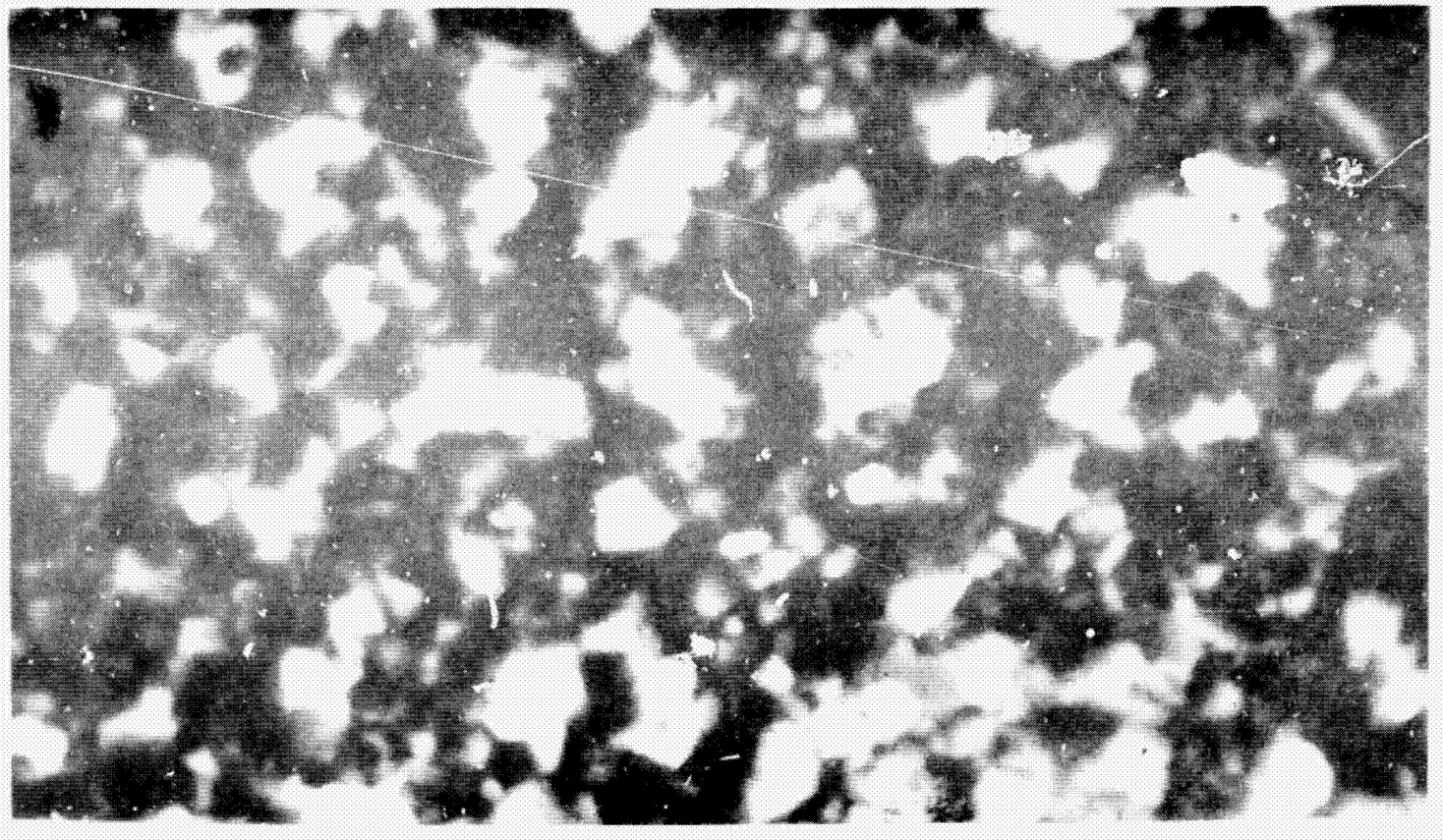
(1) Preparation and characterization of Cu_xS and $CuInS_2$ films on various substrates for photovoltaic cells using sulfurization of deposited Cu and CuIn films.

(2) Investigate cathodoluminescence as a diagnostic tool for identifying Cu_xS and $CuInS_2$ compounds.

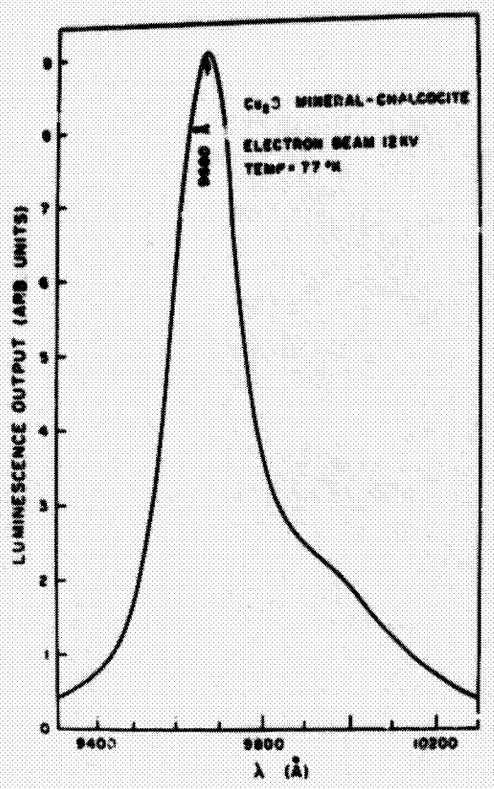
(3) Preparation of single crystals of $CuInS_2$ and p-n junctions

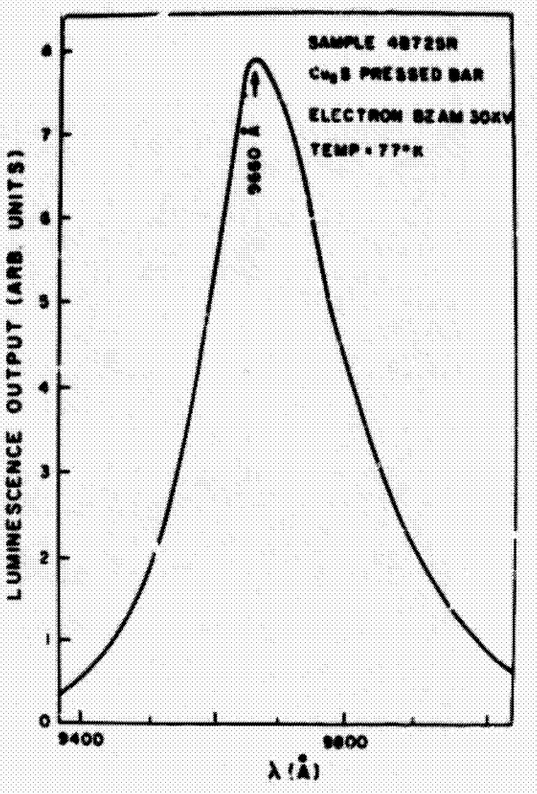


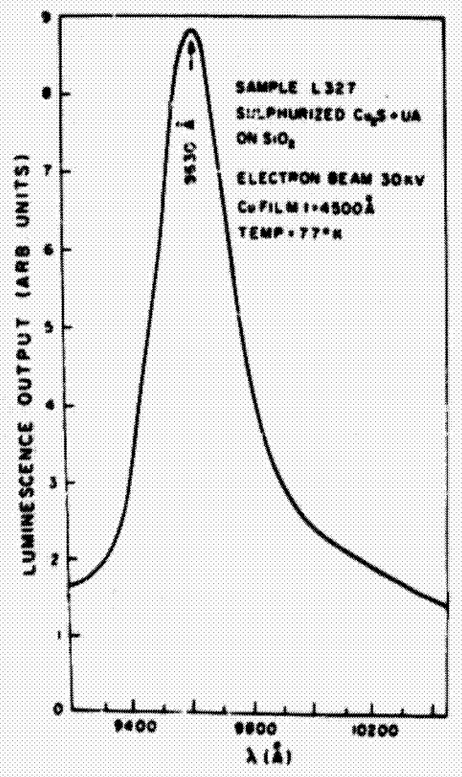


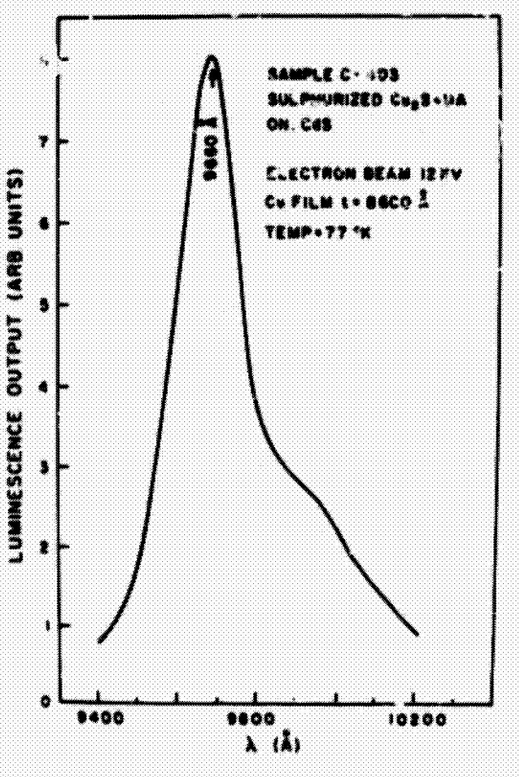


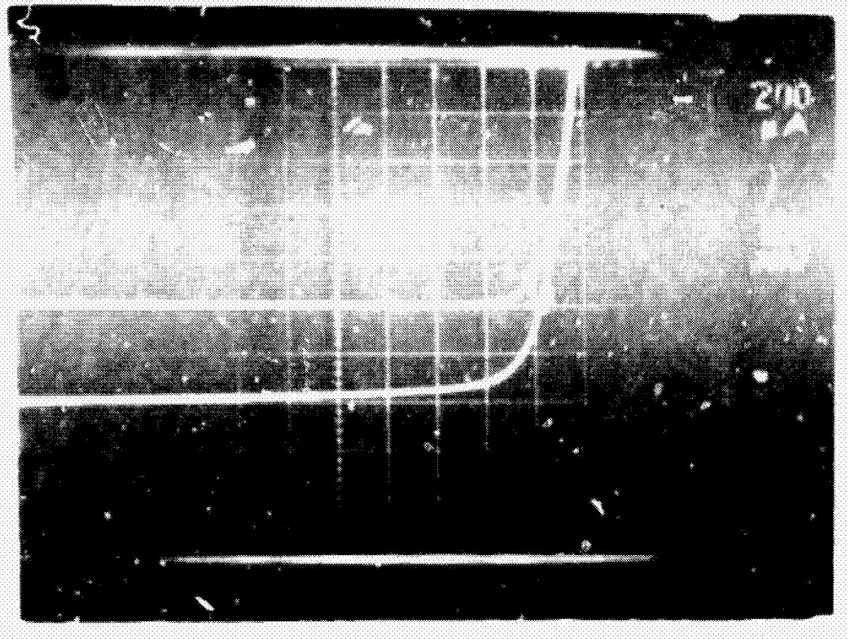
SULFURIZED
4500 Å Cu / 1000 Å AL ON SiO_2


LUMINESCENCE OUTPUT (ARB UNITS)
Cu_2O MINERAL - CHALCOCITE
ELECTRON BEAM 12KV
TEMP = 77°K
9660 Å
9400
9800
10200
λ (Å)

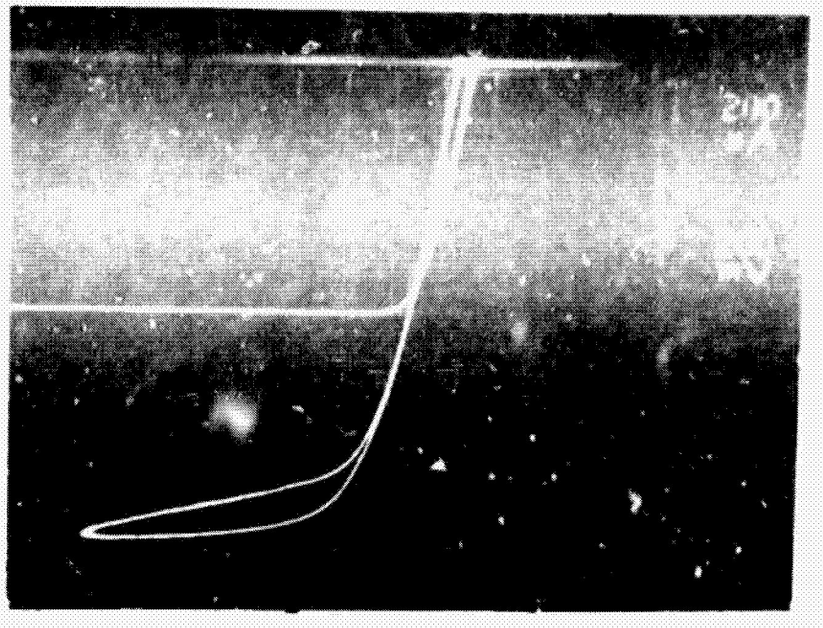

LUMINESCENCE OUTPUT (ARB. UNITS)
SAMPLE 48725R
Cu_2S PRESSED BAR
ELECTRON BEAM 30KV
TEMP = 77°K
9660 Å
9400
9800
λ (Å)


LUMINESCENCE OUTPUT (ARB UNITS)
SAMPLE L 327
SULPHURIZED Cu_2S + UA
ON SiO_2
ELECTRON BEAM 30KV
Cu FILM t = 4500 Å
TEMP = 77°K
9630 Å
9400
9800
10200
λ (Å)


LUMINESCENCE OUTPUT (ARB UNITS)
SAMPLE C - 103
SULPHURIZED Cu_2S + UA
ON. CdS
ELECTRON BEAM 12KV
Cu FILM t = 8600 Å
TEMP = 77 °K
9660 Å
9400
9800
10200
λ (Å)

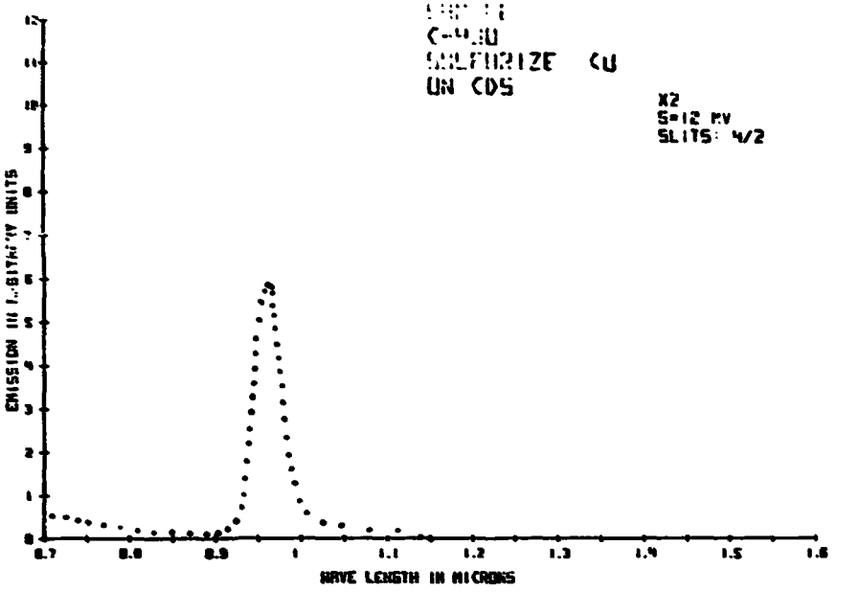


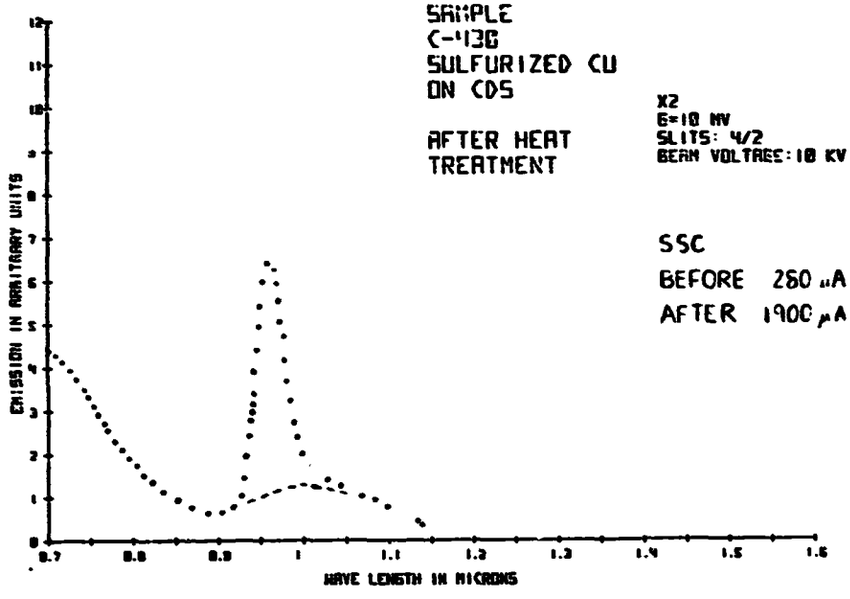
PHOTOVOLTAIC RESPONSE OF DIPPED
Cu_xS-CdS CELL

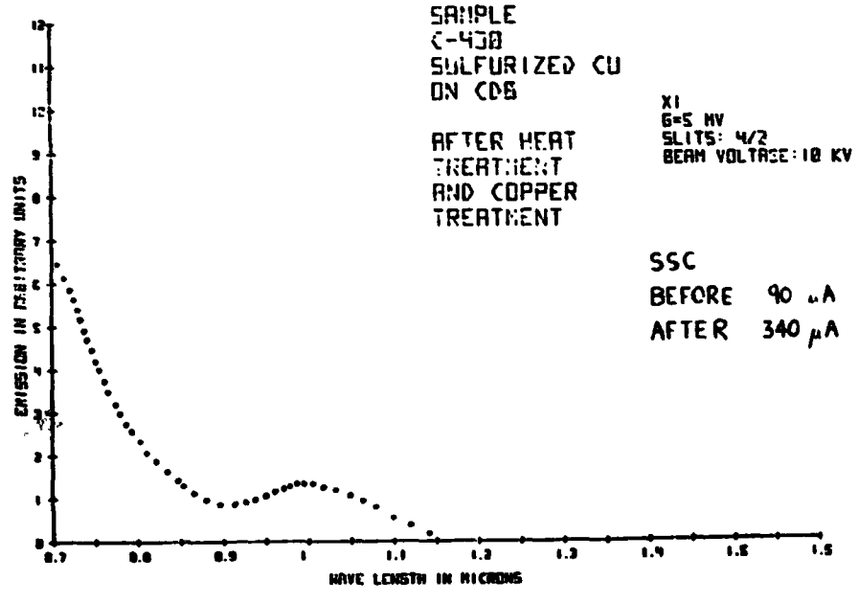


PHOTOVOLTAIC RESPONSE OF SULFURIZED
Cu_xS-CdS CELL

Cell No.	...tment (in air) temp (°C) / time (min)	I_{sc} (ma) Before	I_{sc} (ma) After	increase factor	Copper Treatment (in air)- 60A° temp / time	I_{sc} (ma) Before	I_{sc} (ma) After	increase factor
C 485	200 / 26	0.14	0.60	4.2				
C 525					200 / 10	0.019	0.33	17.0
C 430	200 / 7	0.28	1.9	6.8	200 / 10	0.09	0.40	4.4
C 525-2	180 / 7	0.06	0.45	7.5	200 / 27	0.32	0.60	1.9
C 437	200 / 9	0.75	2.0	2 7	200 / 10	0.34	0.50	1.5


C-430
SULFURIZE CU
ON CDS
X2
G=12 MV
SLITS: 4/2
WAVE LENGTH IN MICRONS


SAMPLE
C-430
SULFURIZED CU
ON CDS
AFTER HEAT
TREATMENT
X2
G=10 MV
SLITS: 4/2
BEAM VOLTAGE: 10 KV
SSC
BEFORE 280 μA
AFTER 1900 μA
EMISSION IN ARBITRARY UNITS
WAVE LENGTH IN MICRONS


SAMPLE
C-430
SULFURIZED CU
ON CDS
AFTER HEAT
TREATMENT
AND COPPER
TREATMENT
X1
G=5 MV
SLITS: 4/2
BEAM VOLTAGE: 10 KV
SSC
BEFORE 90 μA
AFTER 340 μA
WAVE LENGTH IN MICRONS

Summary of results

1) Cu_2S films prepared on Silica, Aluminum, Silicon, CdS - no limitation on substrates.

2) Cathodoluminescence can be used as diagnostic tool to identify Cu_2S and copper impurities.

3) Junctions on CdS and Si exhibit up to 1% η without process optimization.

4) "Heat treatments" and "Cu treatments" can increase SSC by over 1 order of magnitude.

Planned Activity for Next 6 Months

1. Optimize process for sulfurization of Cu on single crystal CdS - objective is cell with $\sim$ 5% efficiency.

2. All thin film cells
   (a) Cu sulfurized on quartz or metal followed by
   (b) Evaporation of semiconductor - CdS or more optimum mate

3. Growth of $CuInS_2$ crystals and Preparation of p-n junctions

4. Refinement of cathodoluminescence diagnostics

5. Co-operation with University of Maine