INVESTIGATION OF THIN FILM SOLAR CELLS
BASED ON
\( \text{Cu}_2\text{S} \) AND TERNARY COMPOUNDS SUCH AS \( \text{CuInS}_2 \)

BROWN UNIVERSITY

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Abstract

The work at Brown University is concerned with the production and characterization in film form of Cu$_2$S and related Cu compounds such as CuInS$_2$ for photovoltaic cells. The low cost process technology being examined, namely the sulfuration 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$_x$S 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$_2$S 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 9000Å of Cu$_x$S is needed to make a positive identification, although films as thin as 4500Å 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 1500Å of Cu$_2$S. 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 (1500Å of Cu yields crystallites of 0.4 μm diameter; 9000Å of Cu$_2$S 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$_2$S 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 Cu₂S. 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 Cu₂S peak is retained but there is a strong background due to either Cu impurities or defects. For Cu treated films, the Cu₂S peak disappears. In the case of Cu treated films, x-rays reveal that Cu₂S is still present but other unidentified lines are also present.

Diodes formed on single crystal CdS have reasonable I-V characteristics with \( V_{oc} \approx 0.45 - 0.5 \) 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 \( \approx 5\% \). 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 CuₓS responsible for the strong photovoltaic effect. In addition we plan to expand our activity on the growth of CuInS₂ crystals and preparation of p-n junctions.
Program Objectives

(1) Preparation and characterization of Cu$_x$S 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$_x$S and CuInS$_2$ compounds.

(3) Preparation of single crystals of CuInS$_2$ and p-n junctions.
PHOTOVOLTAIC RESPONSE OF DIPPED Cu_{x}S-CuS CELL

PHOTOVOLTAIC RESPONSE OF SULFURIZED Cu_{x}S-CuS CELL
<table>
<thead>
<tr>
<th>Cell No.</th>
<th>temp (°C)</th>
<th>time (min)</th>
<th>( I_{sc} ) (ma)</th>
<th>increase factor</th>
<th>temp</th>
<th>time</th>
<th>( I_{sc} ) (ma)</th>
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SAMPLE
C-13B
SULFURIZED CU
ON CdS

AFTER HEAT TREATMENT
X2
E=10 KV
SLITS: 0.2
BEAM VOLTAGE: 10 KV

SSC
BEFORE 250 μA
AFTER 1900 μA

SAMPLE
C-43B
SULFURIZED CU
ON CdS

AFTER HEAT TREATMENT AND COPPER TREATMENT
X1
E=5 KV
SLITS: 0.2
BEAM VOLTAGE: 10 KV

SSC
BEFORE 90 μA
AFTER 340 μA
Summary of results

1) Cu₂S films prepared on Silica, Aluminum, Silicon, CdS - no limitation on substrates.

2) Cathodoluminescence can be used as diagnostic tool to identify Cu₂S and copper impurities.

3) Junctions on CdS and Si exhibit up to 1% 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 ~ 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 CuInS₂ crystals and Preparation of p-n junctions

4. Refinement of cathodoluminescence diagnostics

5. Co-operation with University of Maine