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Barry Lee Chin
(M. S. thesis)

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AN INVESTIGATION OF THE Cu$_x$S/Si PHOTOVOLTAIC CELL

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AN INVESTIGATION OF THE Cu$_x$S/Si PHOTOVOLTAIC CELL

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ABSTRACT

Cu$_x$S/Si heterojunctions were formed in an attempt to verify reported conversion efficiencies of up to 4% for "Cu$_2$S"/Si photovoltaic cells. Various Cu$_x$S/Si cells ($1.8 < x < 2.0$) were made by simultaneous vacuum deposition of copper and sulfur onto (100) single crystal silicon substrates. Since many Cu$_x$S phases exist near the stoichiometric value, the structure of the evaporated films was determined by X-ray analysis. Spectral response measurements were made which were consistent with the X-ray results showing the presence of more than one Cu$_x$S phase in the cells. The measured sunlight conversion efficiencies of these cells were approximately 0.25%, making them impractical for economical photovoltaic use. Reasons for the differences in conversion efficiencies are discussed. It was observed that the efficiencies slowly increased with room-temperature aging. This is explained in terms of the relaxation of lattice defects at the heterojunction interface.
INTRODUCTION

A. Nature of the Problem

The dwindling supply of fossil fuel for the industrialized segments of the world is of primary concern for the continuation of civilized society as we now know it. As humankind becomes increasingly aware of its relationship with the universe, decision-making becomes more crucial as to the path society will follow in the future. The possible solutions to the problem of finding inexpensive alternative energy sources must be weighed in terms of their social consequences as well as to their technical feasibilities. An attractive solution is the utilization of solar energy which has been shown to be efficient in the heating and cooling of homes. The "direct" conversion of sunlight into electricity by the photovoltaic effect is an important area of promising solar energy research.

Single crystal Si photovoltaic cells have been employed effectively as primary power sources for spacecraft missions. Their high cost, however, may never permit their large scale terrestrial use. Another photovoltaic system is the thin-film Cu$_x$S/CdS cell* which is inherently less expensive to produce than the single crystal Si and GaAs cells, but has lower efficiency which has been found to decrease with time. Economic considerations and stability problems of present photovoltaic devices have thus brought attention to alternative solar cell systems.

*The x in Cu$_x$S represents the ratio of copper atoms to sulfur atoms.
Theoretical considerations and information concerning presently efficient devices should provide insight in the selection and capability of other materials for photovoltaic conversion. The importance of Cu$_x$S in the Cu$_x$S/CdS cell has led to the possibility of its use in other heterojunction devices. Cu$_2$S has a high absorption coefficient so that only thin films are required, thus allowing for the use of low cost process technology. Efficiencies of up to 4% have been reported by Drozdov and Mel'nikov$^1$ for p-Cu$_2$S/n-Si photovoltaic devices, creating interest in this heterojunction structure.

The ability to reproduce desired characteristics is necessary before the feasibility of a given photovoltaic cell may be realized. It has been found for Cu$_x$S/CdS cells (in which the Cu$_x$S layer contributes the significant photoresponse) that the cell performance depends strongly upon the composition of the copper sulfide film.$^2$ The Cu-S phase diagram indicates that many phases exist near the stoichiometric composition (Cu$_2$S providing the best photovoltaic characteristics), making the characterization of the Cu$_x$S layer necessary. The aim of this work is to form Cu$_x$S films on Si substrates to gain insight as to the operation of the cell and determine its feasibility for photovoltaic use. The substrate material could possibly be large grained polycrystalline silicon thus avoiding the high cost of growing and slicing large single crystals.

B. Principle of the Photovoltaic Effect

The photovoltaic effect may be described as the appearance of a voltage due to incident photons in the vicinity of a potential barrier.
For a p-n junction only those photons with energies equal to or greater than the bandgap of the semiconductor can lead to the generation of electron-hole pairs. This gives rise to a change in minority carrier densities (assuming that the relative change in majority carrier densities is small with illumination). Electrons in the p-type region which are within a diffusion length, \( L_n \), of the junction can lower their energy by descending the potential barrier to the n-type side as shown in the band diagram of Fig. 1.1. Holes in the n-type material can diffuse to the junction, if within the diffusion length, \( L_p \), and "float" up the potential barrier; the net effect being a measurable potential difference, \( V_o \). Assuming an ideal diode, the open circuit voltage, \( V_{oc} \), is given by

\[
V_{oc} = \frac{kT}{q} \ln \left( 1 + \frac{I_g}{I_o} \right) \tag{1.1}
\]

where

\( k = \) Boltzmann's constant

\( T = \) Temperature

\( q = \) Electronic charge

\( I_g = \) Photocurrent = \( g(L_n + L_p) \) where \( g \) is the generation rate (electron-hole pairs / cm\(^3\)-sec)

\( I_o = \) Reverse saturation current.

The current-voltage relationship for the photovoltaic cell is

\[
I = I_o (e^{eV_{oc}/kT} - 1) - I_g \tag{1.2}
\]

which is plotted in Fig. 1.2(a).
The non-ideal photovoltaic cell, however, has a finite series resistance, $R_s$, and shunt resistance, $R_{sh}$, which modify Eq. (1.2) so that

$$I = I_o \left[ e^{(V_o - IR_s)/kT} - 1 \right] + \frac{V_o - IR_s}{R_{sh}} - I_g.$$  

(1.3)

This corresponds to the equivalent circuit given in Fig. 1.2(b). Due to the conditions $R_s > 0$ and $R_{sh} < \infty$, the maximum power output is not the product $V_{oc}I_{sc}$, but is given by the maximum power rectangle as shown in Fig. 1.2(a). A fill factor, defined as the ratio of the maximum power rectangle to the product of $V_{oc}$ and $I_{sc}$, is used in calculating the cell's efficiency.

A heterojunction, composed of an n- and p-type material with different bandgaps, electron affinities, and crystal structures requires a more complex analysis. An important feature of the band diagram of a heterojunction is the discontinuity which will be present in the conduction and valence bands due to the differences in electron affinities. The reader is referred to a review of the models describing the phenomena at heterojunctions given by Van Ruyven.  

C. Previous Related Research

1. The Copper-Sulfur System

$Cu_2S$ is a degenerate p-type semiconductor with an indirect bandgap of approximately 1.2 eV and a direct bandgap of approximately 1.8 eV as given by the rigid band model proposed by B.J. Mulder. At room temperature, however, several copper sulfide phases exist very close to the stoichiometric chalcocite phase, $Cu_2S$. Cook has completed the most
recent review of the literature along with his results dealing with
the reactions of copper with sulfur. The following is a summary of
stable and metastable $\text{Cu}_x \text{S}$ compounds and phases at room temperature
according to Cook.

**Chalcocite:** $\text{Cu}_2 \text{S}$ is a common sulfide ore with limited solid
solubility. The compound has been described as orthorhombic
with $a = 11.84$, $b = 27.33$, and $c = 13.49$. The structure of
the low temperature orthorhombic form consists of ordered
copper atoms in a slightly distorted hexagonal close-packed
sulfur matrix.

**Djurleite:** $\text{Cu}_{1.96} \text{S}$ named for the discoverer of the compound$^7$
is orthorhombic with $a = 31.42$, $b = 13.56$, and $c = 26.84$. It
was established by Cook that the true composition of djurleite
is $\text{Cu}_{1.93} \text{S}$ with the sulfur atoms in the same packing arrangement
as for chalcocite.

**Digenite:** $\sim \text{Cu}_{1.8} \text{S}$ is pseudocubic with a composition range which
is still a subject of discussion. The cubic close-packed sulfur
arrangement was found for this phase.

**Covellite:** $\text{CuS}$ has a hexagonal structure with $a = 3.79$ and
$c = 16.33$. It deviates from stoichiometry by $< \pm 0.001$.

**Other Phases:** $\text{Cu}_{1.9} \text{S}$ as reported by Eliseev, et al.$^8$ is a
hexagonal phase with $a = 11.35$ and $c = 13.50$. Cook was doubtful
of its existence since no one else had obtained this phase.
However, at least two other studies$^9,10$ have reported data
about this phase. A phase for which there is no confirmation
as to its stability is the tetragonal \( \text{Cu}_x \text{S} \) (1.8 < \( x \) < 1.93) which was obtained by chemical conversion of cadmium sulfide to cuprous sulfide. Both \( \text{Cu}_{1.91} \text{S} \) and \( \text{Cu}_x \text{S} \) are expected to have a hexagonal close packed sulfur arrangement.

The phase diagram for \( \text{Cu}_{2.0} \text{S} \) to \( \text{Cu}_{1.72} \text{S} \) is thus given in Fig. 1.3 as determined by Cook.

2. The \( \text{Cu}_x \text{S}/\text{Si} \) Photovoltaic Cell

Drozdov and Mel'nikov\(^1\) reported results obtained with heterojunctions prepared by thermal sublimation of \( \text{Cu}_2 \text{S} \) powder ("analytic purity") onto (111) silicon substrates. Their investigation produced cells with open circuit voltages of up to \( \sim 0.6 \) V and short-circuit currents of up to \( \sim 40 \) mA/cm\(^2\), with efficiencies of the better samples ranging up to 4%. The reported spectral response measurements indicated that the photosensitivity extended from 0.4 to 2.0 \( \mu \) which they attributed to cuprous sulfide and silicon contributions. However, the photosensitivity of these heterojunctions are beyond the fundamental absorption edges of cuprous sulfide and silicon. They found the spectral sensitivity of their cells to depend on the method used to deposit the cuprous sulfide film, particularly the evaporator temperature. This raises the question as to the actual components of the heterojunction examined in their study.

To study cells based on \( \text{Cu}_2 \text{S} \), J.J. Loferski and his group at Brown University\(^1\)\(^2\) have developed a technique involving the sulfurization of evaporated copper films on CdS and Si. By adjusting the sulfur partial pressure in a flowing mixture of hydrogen sulfide, argon
and hydrogen over the evaporated layers, various phases of the Cu-S system were produced. By varying the sulfurization parameters largely Cu$_2$S films, as determined by X-ray analysis and cathodoluminescence, were formed on (111) and (110) Si wafers, with no differences observed. The efficiency of such cells was less than 1% (the results of one cell showed $V_{oc} \sim 0.125$ V, $I_{sc} \sim 250$ µA, the area of the cell was not given). X-ray data indicated for Si substrates that an additional phase was present. This was interpreted as a phase of the Cu-Si-S system that formed as a result of the rapid diffusion of Cu into Si. A diffusion barrier was introduced by growing a thin oxide layer (60-100 Å) on the Si surface before the copper evaporation. Cu$_2$S prepared on such an oxide surface did not show the presence of any Cu-Si-S interfacial alloy layer. The oxide interface diodes showed an increase in $V_{oc}$ (~50%), attributed to the increased barrier height of the SiO$_2$ interface, but led to a decrease in $I_{sc}$ (~0.2 mA/cm$^2$). The workers remarked that the 2% lattice mismatch in the Cu$_2$S/Si interface may cause this system to be always weak.

3. **The Cu$_2$S/Si Energy Band Diagram**

Based on measurements of their evaporated films, Drozdov and Mel'nikov constructed an energy band diagram as shown in Fig. 1.4(a). From capacitance-voltage measurements a diffusion potential of 0.8 eV was determined from which the electron affinity of the cuprous sulfide was estimated as ~3.76 eV. The band gap of the cuprous sulfide was determined by the temperature dependence of the conductivity of the film and was found to be 1.84 eV. From the band gap and electron affinity of Si the final band diagram obtained indicated a conduction band
discontinuity of ~0.74 eV and no discontinuity in the valence band.

Loferski, et al.\textsuperscript{13} constructed a Cu\textsubscript{2}S/Si band diagram as shown in Fig. 1.4(b) by assuming the electron affinity of Cu\textsubscript{2}S to be close to that of Si (this was based on the similarity of the CdS-Si solar cell to the CdS-Cu\textsubscript{2}S cell\textsuperscript{14}). The band diagram then resembled that of a homojunction except for a discontinuity in the valence band. The diffusion potential was determined to be ~1.0 eV.

In analyzing the two proposed diagrams one should note the differences in bandgaps of the cuprous sulfides, suggesting that the same heterojunction was not being examined. Both studies, however, determined that a diffusion potential between 0.8 and 1.0 eV could be expected, giving promise of a reasonable open-circuit voltage.
II. EXPERIMENTAL PROCEDURE AND APPARATUS

A. Vacuum Deposition Method

To vary the thickness and composition of the evaporated Cu\textsubscript{x}S film, a two source resistive-heated vacuum deposition apparatus was constructed as shown in Fig. 2.1. The five substrate positions allow for different path lengths for the evaporating copper and sulfur atoms. The height of the substrate holder, h, was set at 20 cm, intersource separation was 3.5 cm, and the individual exposed substrate areas were \( \sim 2 \text{ cm}^2 \). The aluminium substrate holder temperature was monitored by an iron-constantan thermocouple mounted on the face directed towards the vapor sources. The evaporant materials were 99.9% pure copper shot (Orion Chemical Co.) and \( \sim 95\% \) pure chunk sulfur (Allied Chemical). The depositions were conducted at base pressures of approximately \( 2 \times 10^{-6} \text{ Torr} \) using a conventional liquid-nitrogen-trapped diffusion-pumped system.

It was hoped that the film resulting from the simultaneous evaporation of copper and sulfur would be the summation of the individual contributions given by the point source approximation (thickness proportional to [source-to-substrate distance]\(^{-2}\)). A variation in composition with substrate position would then be expected with films at position \#1 (above the Cu source) to be copper-rich with respect to position \#5 (above the S source). Individual evaporations of Cu and S onto glass substrates were conducted and the thickness of these films measured by multiple beam interferometry to test this proposal.
The final deposition parameters were varied to produce Cu$_x$S$_y$ films on Si substrates. The Cu and S sources were heated until evaporation was observed to proceed at which time the shutter was opened. For Cu mass \(\sim 0.9\) g and S mass \(\sim 0.1\) g the times for evaporation were approximately 3 and 1.5 minutes respectively. A rise in base pressure of less than \(6 \times 10^{-6}\) Torr was usually observed during this process. The substrate holder initially at room temperature increased \(\sim 20^\circ\)C. The thickness of the Cu$_x$S$_y$ films on Si was measured by a Clevite Model 150 Surfalyzer.

B. X-Ray Diffraction Measurements

To identify the Cu$_x$S$_y$ phases deposited on glass and Si substrates, x-ray scans (2$\theta$=20° to 2$\theta$=55°) of these films were performed on a Picker Model 3488K diffractometer using Cu K$_\alpha$ radiation. Measured d-spacings and their relative intensities were correlated with reported values. To determine if the films had a preferred orientation, the diffractometer counter was fixed at a strong Bragg reflection and the sample then rotated about the diffractometer axis. The relative intensity of the peak was examined with rotation of the specimen. No change in the relative intensity would indicate a randomly oriented sample.

C. Sample Preparation

The Si wafers used in this study (obtained from Semimetals, Inc.) had the following specifications: (100) orientation, doped with phosphorous, resistivity \(\sim 0.22\ \Omega\cdot\)cm and thickness \(\sim 0.35\) mm. One side of the wafer was lapped while the other surface was polished to a
mirror finish by an industrial mechanical and chemical technique. The wafers were scribed and broken to the dimensions 1.85 cm \times 1.35 cm to allow for an evaporated film area of \sim 2 \text{ cm}^2 (to provide maximum X-ray beam exposure). Ohmic contact to Si was made by "sparking". In electrodes (99.999\% pure In wire) onto the lapped surface of the samples as described by Flores.\textsuperscript{15} The apparatus used for this process is shown in Fig. 2.2(a). The current-voltage linearity of these contacts were examined at room temperature and found to be very good.

Before deposition of the Cu\textsubscript{x}S film onto the polished side of the samples, the specimens were etched in \sim 10\% concentration HF for 30 seconds to remove the oxide layer. It was found that the etchant did not attack the In contacts. After deposition, electronic grade silver paint was used as the conduction medium between the In contacts and a copper substrate. Silver paint was also used as the ohmic front contact to the Cu\textsubscript{x}S film as shown in Fig. 2.2(b) of the completed cell.

\textbf{D. Current-Voltage Characteristics}\textsuperscript{16}

Cell I-V characteristics were measured with a Tektronix Type 502 A oscilloscope and a Waveforms 401 H sine wave generator in the circuit as shown in Fig. 2.3. Tests were performed in sunlight on clear days at Lawrence Berkeley Laboratory with the cells positioned for optimum exposure. A tracking pyranometer located at the laboratory indicated that an average insolation of 100 mW/cm\textsuperscript{2} could be expected.\textsuperscript{17} This value was assumed for all calculations.
E. Spectral Response Characteristics

The spectral response measurements were carried out with the set-up illustrated in Fig. 2.4. The quartz-halogen lamp supply was always adjusted for a lamp current of 6 amperes. An Oriel Model 7240 monochromator with a 750 mm blaze, 1200 l/mm grating, and 1.8 mm slits which give a 12 nm bandpass was used. The monochromator output versus wavelength was determined with a Hewlett-Packard Model 8330A radiant flux meter with an 8334A thermopile detector. The short-circuit current was measured with a Keithley 602 electrometer. In the open-circuit mode the load on the cell was $> 10^{11} \Omega$; and in the short-circuit mode the voltage drop was $< 1.0$ mV. The flux meter readings were then used to normalize the short-circuit current to constant incident intensity, assuming the short-circuit to be proportional to incident intensity.
III. EXPERIMENTAL RESULTS

A. Film Formation

The measured thickness of copper-evaporated films for the various substrate positions agreed well with the value given by the point source thickness distribution:

\[ t = \frac{m \cos \theta}{4\pi \rho r^2} \]  

(3.1)

where \( m \) is the mass of the charge evaporated, \( \theta \) is the angle between the normal to the substrate and the path of the incoming atom, \( \rho \) is the density of the material evaporated, and \( r \) is the source-to-substrate distance. The thickness of the sulfur films, however, was measured to be much less than that calculated by the above relationship, suggesting either a low sticking coefficient or a high surface mobility of the S atoms.

To determine which of these two mechanisms was working, two Cu plates (one of which was shielded) and a long Cu plate (one end of which was shielded) were exposed to evaporating S atoms as shown in Fig. 3.1. If the nonadherence of the S atoms was due to high surface mobility, then no Cu \(_x\) S film could be expected to form on the completely shielded plate since the plates were suspended by thin wires. It was found that all surfaces of the exposed and shielded regions formed a Cu \(_x\) S film, implying a low sticking coefficient. This also indicated that S atoms were arriving from all directions as they "bounced-off"
surfaces in the vacuum system. With these considerations taken into
account, the deposition parameters were varied so that $\text{Cu}_x\text{S}_y$ films were formed. For the cells examined in this study the thickness of the $\text{Cu}_x\text{S}_y$ layers on Si was determined to be $\sim 3000 \, \text{Å} \, (\pm 250 \, \text{Å})$.

B. X-Ray Diffraction Measurements

Measured d-spacings from the evaporated films on Si substrates were compared with powder pattern values for the pure components Cu and S and the possible binary and ternary phases composed of Cu, S, O and Si. X-ray measurements and identification of three films on Si (forming Cells 8/13.1, 8/13.3, and 8/22.3) as determined immediately after evaporation are given in Table 1. It was found by the procedure described in Section II.B that these films had a preferred orientation which accounts for the differences in measured and reported relative intensities (the ASTM powder pattern intensities are given for randomly oriented grains). Note that the data show a mixture of phases present. To determine if any phase transformations occurred with time, X-ray scans were performed at later times. The samples were kept in a desiccator exposed to room light between testings. The same Bragg reflections were observed after subsequent aging at room temperature.

C. Current-Voltage Measurements

Current-voltage characteristics of the cells examined in this study showed that the measured efficiencies (all $< 0.25\%$) differed with the copper sulfide phases forming the p-type layer. Correlation between efficiency and composition of these films is difficult because of the unknown contribution of each phase present in the mixture to
Table 1. X-Ray Diffraction Pattern of:

<table>
<thead>
<tr>
<th>Measured</th>
<th>Cu$_{1.8}$</th>
<th>Cu$_{1.93}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>I/I$_0$</td>
<td>d(Å)</td>
</tr>
<tr>
<td>3.75</td>
<td>15 (40)*</td>
<td></td>
</tr>
<tr>
<td>3.20</td>
<td>10</td>
<td>3.21</td>
</tr>
<tr>
<td>2.77</td>
<td>100</td>
<td>2.77</td>
</tr>
<tr>
<td>1.95</td>
<td>38 (100)</td>
<td></td>
</tr>
<tr>
<td>1.87</td>
<td>23 (60)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measured</th>
<th>Cu$_{1.91}$</th>
<th>Cu$_{1.93}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>I/I$_0$</td>
<td>d(Å)</td>
</tr>
<tr>
<td>3.26</td>
<td>33</td>
<td>3.26</td>
</tr>
<tr>
<td>3.18</td>
<td>52 (100)</td>
<td></td>
</tr>
<tr>
<td>3.02</td>
<td>33 (63)</td>
<td></td>
</tr>
<tr>
<td>2.87</td>
<td>43 (82)</td>
<td></td>
</tr>
<tr>
<td>1.94</td>
<td>30 (57)</td>
<td></td>
</tr>
<tr>
<td>1.89</td>
<td>100</td>
<td>1.89</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Measured</th>
<th>Cu$_x$</th>
<th>Cu$_{1.765}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>I/I$_0$</td>
<td>d(Å)</td>
</tr>
<tr>
<td>3.18</td>
<td>30 (64)</td>
<td>3.19</td>
</tr>
<tr>
<td>2.86</td>
<td>100</td>
<td>2.86</td>
</tr>
<tr>
<td>2.76</td>
<td>35 (75)</td>
<td>2.77</td>
</tr>
<tr>
<td>1.95</td>
<td>47 (100)</td>
<td>1.96</td>
</tr>
</tbody>
</table>

*The values in parentheses are the relative intensities of the phase in lower concentration.
the overall properties of the cell. Also, the effect of lattice mismatch between the different phases and with the silicon interface should not be neglected. With room-temperature aging, increases in the open-circuit voltage of all three cells were observed, as seen in Figs. 3.2, 3.3, and 3.4. The change in efficiency with aging time is shown in Fig. 3.5. To ascertain what process could account for these changes, the light generated current and the logarithm of the reverse saturation current were plotted against aging time in Figs. 3.6 and 3.7, respectively. It is seen that $I_g$ does not change, however, $I_o$ decreases as $\exp(-\text{time})$. In all these calculations a solar radiation of 100 mW/cm$^2$ has been assumed which could account for some of the errors involving parameters which are a function of the level of illumination (a deviation of 10% from this value can be expected due to changes in the position of the sun$^{17}$). It was also assumed that light scattered behind the front contacts does not contribute to the total current.

D. Spectral Response Measurements

Given in Figs. 3.8 through 3.10 are the linear plots of short-circuit current versus wavelength for the cells studied. The responses appear to be the superposition of two different absorption curves, supporting the X-ray analysis determination of two phase mixtures. There is no response at longer wavelengths corresponding to band transitions in Si, suggesting total absorption in the Cu$_x$S layer. The maxima of the responses provide a qualitative test for identification of the Cu$_x$S phases present in each of the cells. The phase in
higher concentration can be assumed to give rise to the larger maximum in the spectral response curve if the absorption coefficients of the various phases are approximately the same.

B. J. Mulder\textsuperscript{10} found for \( \text{Cu}_x \text{S} \) phases with \( 1.8 < x < 2.0 \) that for a given photon energy the absorption coefficient decreased with lower copper concentration. A shift in the band edge to higher energies with lower copper-content phases was also reported. Taking into account these results, the spectral response curves lend further confirmation for the identification of the phases as determined by X-ray analysis; e.g. for Cell 8/13.1 the relative higher concentration of \( \text{Cu}_{1.8} \text{S} \) may correspond to the larger response at shorter wavelengths, with \( \text{Cu}_{1.93} \text{S} \) response at the longer wavelength maximum. Spectral response measurements taken at later dates showed no shift in spectral sensitivity.
IV. DISCUSSION

The measured efficiencies and spectral response curves from the work of Drozdov and Mel'nikov on "Cu₂S"/Si photovoltaic cells could not be duplicated in this study. Conversion efficiencies of approximately 0.25% were found for mixtures of copper sulfide phases on (100) silicon substrates. Although no chalcocite was formed (or if Cu₂S was deposited the chalcocite to djurleite transformation was rapid), results from Loferski, et al. indicated low efficiencies for the Cu₂S/Si cell (the chalcocite phase determined by X-ray analysis and cathodoluminescence). Other results which question the findings of Drozdov and Mel'nikov are:

(1) Their thermal sublimation of cuprous sulfide powder could have resulted in the partial separation of the components. Using thermodynamic relations compiled by Cook, it was determined that the vapor pressure of sulfur is approximately twice as high as that of Cu₂S at their reported evaporator temperature of 1500°C. Variations in Cu₅S₇ phase can then be expected, possibly explaining the different spectral responses observed with changes in their evaporator temperature.

(2) Films formed from the evaporated "Cu₂S" powder were reported to be 1-5 μ thick, thus requiring a large minority carrier diffusion length to prevent recombination before reaching the junction. Gill and Bube, however, have placed an upper limit of about 0.4 μ for the minority carrier diffusion
length for copper sulfide (no determination of the Cu$_x$S phase measured was made). Absorption was found to be complete in an ~3000 Å thick film in this study.

(3) The spectral response curve was not consistent with the proposed heterojunction structure. It would appear that a Cu$_2$S/Si heterojunction was not formed but rather a different barrier cell. The measured bandgap of 1.84 eV for the evaporated film indicates that chalcocite (with an indirect bandgap of 1.2 eV) was not deposited but possibly another copper sulfide phase or even an interfacial layer composed of Cu-Si was formed.

(4) The activation energy of acceptors (excess sulfur atoms) was reported as 0.17 eV above the valence band edge. Okamoto and Kawai\textsuperscript{21} found that Cu$_x$S (1.8$\leq x \leq$ 2.0) is a p-type degenerate semiconductor in which the copper vacancies act as acceptors. Their results also showed that the thermoelectric power at 20°C varied from a value of 60 µV/degree for Cu$_{1.99}$S to 18 µV/degree for Cu$_{1.8}$S. The value for the evaporated "Cu$_2$S" film was 1.25 µV/degree, not even falling within the chalcocite to digenite region.

Therefore, the structure giving rise to the 4% conversion efficiencies does not appear to be a Cu$_x$S/Si (1.8$< x <$ 2.0) heterojunction. The results of Drozdov and Mel'nikov, however, are still important if the actual components of their cell could be determined and reproduced to give the reported efficiencies.
It was observed that the efficiencies of the cells formed in this study increased slowly with room-temperature aging. Since neither a change in the X-ray data nor a shift in spectral sensitivity was observed at different aging times, a phase transformation of the Cu$_x$S film could not account for the change in efficiencies. The reverse saturation current, however, was found to decrease as $\exp(-\text{time})$. The contributions to $I_o$ are the generation of electron-hole pairs in the depletion region of the junction, called the generation current, and diffusion of generated electron-hole pairs in the bulk of the material, called the diffusion current. For a homogeneous material in which $p_{no} \gg n_{po}$ and $|V| > 3kT/q$, the reverse current density is given by\cite{22}

$$J_R = q \sqrt{D_p \frac{\eta_i^2}{\tau_p n_D}} + q \frac{\eta_i W}{\tau_e}$$

(4.1)

Diffusion current  Generation current

where

- $p_{no}$ = equilibrium concentration of holes in the n-type material
- $n_{po}$ = equilibrium concentration of electrons in the p-type material
- $D_p$ = diffusion coefficient for holes
- $\tau_p$ = lifetime of hole
- $\eta_i$ = intrinsic carrier concentration
- $W$ = depletion-layer width
- $\tau_e$ = effective lifetime $\propto$ (Trap Density)$^{-1}$. 
For small values of the intrinsic carrier concentration (which is true for Si and Cu$_x$S because of their relatively large bandgaps), the generation current will dominate. For this case the reverse saturation current is then proportional to the total density of traps in an effective trapping region at the interface. A decrease in the trap density would lead to an increase in open-circuit voltage as given by Eq. (1.1), thus increasing the conversion efficiency of the cell.

If the trap density is proportional to $\exp(-n\text{time})$ then the decrease in the reverse saturation current may be explained by relaxation of lattice defects at the interface. Oldham and Milnes$^{23}$ have found that the dislocation array accommodating the lattice mismatch at a heterojunction will have pronounced effects on the junction current-voltage characteristics. The core of the dislocations may act as carrier trapping and recombination sites, so that a restructuring of the atoms at the interface (possibly from the motion of dislocations) may explain the observed changes in $I_0$ and hence, conversion efficiencies.
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REFERENCES


16. This apparatus was assembled and tested by Dr. Terry Peterson.

17. Dr. Donald Grether of the Energy and Environment Division at Lawrence Berkeley Laboratory, Personal communication.


19. The relations given by Cook in Ref. 6 (p.29) are:

\[ \log P_{S_2} = - \frac{14500}{T(\text{K})} + 4.60 \text{ above } 430^\circ \text{(atm)} \]

and

\[ \log P_{\text{Cu}_2\text{S}} = - \frac{7687}{T(\text{K})} + 3.37 \text{ (mm Hg)} \]


FIGURE CAPTIONS

Fig. 1.1. Energy band diagram of a p-n homojunction illustrating the photovoltaic effect where $E_F$ represents the Fermi level for the equilibrium condition. Photons with energies, $h\nu$, greater than the bandgap, $E_g$, will excite electrons from the valence band to the conduction band. The continuous and dotted lines represent the band edges in the dark and under illumination, respectively. In the open-circuit condition the separation of the minority carriers produces a voltage, $V_0$.

Fig. 1.2. (a). Current-voltage characteristics of a photovoltaic cell in the dark and under illumination. $I_o$ is the reverse saturation current and $I_g$ the light-generated current. $V_{oc}$ and $I_{sc}$ are the open-circuit voltage and short-circuit current, respectively and the maximum power is given by the product of $V_{max}$ and $I_{max}$.

(b). Equivalent circuit diagram for photovoltaic cell with series resistance, $R_s$, and shunt resistance, $R_{sh}$.

Fig. 1.3. Phase diagram from $Cu_{2.0}^S$ to $Cu_{1.72}^S$ according to Cook (Ref.6).

Fig. 1.4. (a). "$Cu_2S"/Si energy band diagram according to Drozdov and Mel'nikov (Ref.1). $E_c$ and $E_v$ represent the conduction band edge and valence band edge, respectively. The bandgap and electron affinity of "$Cu_2S"$ are 1.84 eV and 3.76 eV, respectively, and for Si 1.1 eV and 4.5 eV. A discontinuity of 0.74 eV for the conduction band is indicated. A diffusion
potential of 0.8 eV was measured and the acceptor level placed 0.17 eV above the valence band edge for "Cu₂S".

(b). Cu₂S/Si energy band diagram according to Loferski, et al. (Ref.13). The electron affinities, χ, of Cu₂S and Si were assumed to be the same and equal to 4.05 eV. The bandgap of Cu₂S is shown as 1.2 eV with a discontinuity in the valence band ΔV=0.1 eV. The diffusion potential is V_D=1.0 eV for moderately doped silicon (the donor level is 0.2 eV below the conduction band edge).

Fig. 2.1. Two-source vacuum deposition apparatus. The source-to-substrate distance, r, could be varied by changing the height of the substrate holder, h, and the position of the substrate.

Fig. 2.2. (a). Schematic diagram of apparatus used for "sparking" in contacts onto silicon.

(b). Cu₂S/Si photovoltaic cell configuration.

Fig. 2.3. Schematic diagram of I-V measurement apparatus.

Fig. 2.4. Schematic diagram of spectral response measurement apparatus.

Fig. 3.1. (a). Positions of exposed and shielded Cu plates to evaporating S atoms.

(b). Position of Cu plate (one end of which is shielded) to evaporating S atoms.

Fig. 3.2. (a). I-V characteristics of Cell 8/13.1 in sunlight (2:00 PDT, 8/20/75, aging time of 7 days).

(b). As in (a) but with aging time of 100 days (12:10 PDT, 11/21/75).
Fig. 3.3. (a). I-V characteristics of Cell 8/13.3 in sunlight
(2:30 PDT, 8/20/75, aging time of 7 days).
(b). As in (a) but with aging time of 62 days (2:45 PDT, 10/14/75).

Fig. 3.4. (a). I-V characteristics of Cell 8/22.3 in sunlight
(1:50 PDT, 8/22.3, aging time of 1 day).
(b). As in (a) but with aging time of 91 days (12 PDT, 11/21/75).

NOTE: For Figs. 3.3, 3.4, and 3.5 the changes in current density scale are due to the addition of another front contact after initial testing.

Fig. 3.5. Conversion efficiencies versus aging time for Cells 8/13.1, 8/13.3, and 8/22.3.

Fig. 3.6. Light-generated current, I_g versus aging time.

Fig. 3.7. Reverse-saturation current, I_o versus aging time (Error bars indicate errors in readings).

Fig. 3.8. Short-circuit current of Cell 8/13.1 versus wavelength of constant intensity incident light.

Fig. 3.9. Short-circuit current of Cell 8/13.3 versus wavelength of constant intensity light.

Fig. 3.10. Short-circuit current of Cell 8/22.3 versus wavelength of constant intensity light.
Electron Energy

P-type

N-type

Excess Electrons

Dark → Light

Excess Holes

Fig. 1.1.
Fig. 1. The graph illustrates the relationship between current (I) and voltage (V) for a photovoltaic cell in both dark and light conditions. The figure shows:

- Dark: Current (I₀)
- Light: Current (I_max)
- Open Circuit Voltage (V₀)
- Maximum Power Output (V_max)

The circuit diagram (b) includes:

- Source resistance (Rₛ)
- Load resistance (Rₛh)
- Current source (I₉)

(b) XBL 7512-9254

Fig. 1.2.
Fig. 1.3.
Fig. 1.4.
Fig. 2.1.
Silver Paste Contacts

(100) Si (~0.35 mm) -

Cu Substrate

Cu$_x$S Film (~3000 Å)

Fig. 2.2.
Fig. 2.4.
Fig. 3.1.
Fig. 3.2.
Fig. 3.3.

(a)

Horizontal Scale: 50 mV/div
Vertical Scale: 5 mA/div
(3.6 mA/cm²-div)

(b)

Horizontal Scale: 50 mV/div
Vertical Scale: 2 mA/div
(1.7 mA/cm²-div)
Fig. 3.4.

(a)

Horizontal Scale: 50 mV/div
Vertical Scale: 10 mA/div
(5.9 mA/cm²-div)

(b)

Horizontal Scale: 50 mV/div
Vertical Scale: 5 mA/div
(4.1 mA/cm²-div)
Fig. 3.5.
Fig. 3.6.
Fig. 3.7.
Fig. 3.8.

SPECTRAL RESPONSE OF CELL B/13.1

SHORT-CIRCUIT CURRENT (REL. UNITS)

WAVELENGTH (NM)
SPECTRAL RESPONSE OF CELL 8/13.3

Fig. 3.9.
SPECTRAL RESPONSE OF CELL 8/22.3

Fig. 3.10.
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