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ABSTRACT

A description is given on the preparation of CuInSe_2 thin films by simultaneous elemental evaporation onto heated alumina substrates using Electron Impact Emission Spectroscopy (EIES) to control Cu and In vaporization rates. The formation of single phase, chalcopyrite structure, P-type CuInSe_2 film material with a polycrystalline grain size slightly under one micron is reported.

The preparation, application, and properties of In deficient selenide films is discussed.

RF sputtered Mo films are described as an acceptable low-cost metallization approach for CdS/CuInSe_2 thin film cells.

Finally, the results of retesting of Boeing's highest efficiency CdS/CuInSe_2 thin film cell after eight months storage are reported which indicate excellent cell stability.

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1.0 SUMMARY

In order to improve process reproducibility, an EIES (Electron Impact Emission Spectroscopy) film deposition controller has been acquired and installed for monitoring/controlling the vaporization rates of Cu and In during the preparation of CuInSe_2 thin films. The application of the EIES unit necessitated a complete revision of the earlier vapor source structures for Cu, In, and Se. Instead of a heated vapor mixing chamber for Cu and In and a coaxial ring for Se, the newly developed configuration, which is compatible with the EIES controller, consists of crossed tungsten boats for Cu and In and two boats for Se. Good deposited film uniformity, better process reproducibility, and much improved system reliability have been achieved with the more recent selenide deposition method. Single phase chalcopyrite CuInSe_2 films have been prepared with electrical properties quite similar to those produced previously with the heated chamber approach. Grain size has, however, been found to be somewhat smaller, i.e., under one micron.

Selenide films deficient in In have been deposited between the cell metallization and the stoichiometric CuInSe_2 as an approach towards minimizing the amount of In contained in the cell, simplifying the formation of an ohmic contact, and achieving the effects of a back surface field. Such low resistivity, P-type films deposited at the standard 450°C substrate temperature have, however, been found to display an undesirable nodular growth characteristic which would prevent their application to cell fabrication.

A procedure for analyzing the elemental composition of the evaporated CuInSe_2 thin films has been established based upon EDAX measurements with an electron microprobe instrument. Two selenide films of widely different electrical properties have been analyzed and again demonstrate the high sensitivity of this material to composition.

RF sputtered molybdenum films have been successfully developed as a low-cost, high conductivity, stable, and ohmic contact metallization for the CdS/CuInSe_2 thin film cells on polycrystalline alumina substrates.

An advanced cell structure has been designed to accommodate several concepts for cell improvement. The low-cost cell metallization, selenide film composition gradients, and selected region In doping of the CdS layer have been included in the design.

A comparison of the photoresponse of Boeing's highest efficiency CdS/CuInSe₂ thin-film cell after nearly eight months storage in normal laboratory environment to the initial response has indicated no measurable degradation in cell properties.

2.0 INTRODUCTION

This is the first quarterly report of work on "Cadmium Sulfide/Copper Ternary Heterojunction Cell Research", SERI Contract XJ-9-8021-1. The copper ternary is the semiconductor compound copper indium diselenide (CuInSe_2) and was the subject of two prior research programs^(1,2). For the current program, the objective is to continue the development of a large area, low cost, stable, polycrystalline thin-film photovoltaic solar cell based upon the CdS/CuInSe_2 material system. The program is directed towards achieving, at the earliest possible time, a 10% efficient thin-film cell on low cost substrates by low cost fabrication methods. Accordingly, the technical approach is to improve the performance and fabrication economics of earlier developed cells produced by vacuum evaporation techniques (simultaneous elemental evaporation for CuInSe_2) onto inexpensive substrates. The specific research tasks include:

- 1) Investigating cell designs and film preparation procedures which would minimize the amount of the rather rare and expensive In contained in the cell structure;
- 2) Developing a low cost cell metallization system;
- 3) Investigating the use and effect of graded selenide films on the cell characteristics;
- 4) Conducting a detailed analysis of the CdS/CuInSe_2 cell properties; and
- 5) Continuing development of a cell conceptual model.

The first reported experimental example of a CdS/CuInSe_2 heterojunction solar cell was fabricated using a single crystal of CuInSe_2 and a vacuum deposited CdS film⁽³⁻⁵⁾. This single crystal device exhibited a uniform photovoltaic quantum efficiency of 70% between wavelengths of 0.55 to 1.25 microns. For an incident solar intensity of 92 mW/cm^2 , the device produced a photocurrent of 38 mA/cm^2 , an open circuit voltage of 0.55V, and a conversion efficiency of 12%. Other than the Si, GaAs, and InP/CdS semiconductor systems, this is the only case of a photovoltaic device with a demonstrated efficiency greater than 10%.

Following the development of a single crystal cell, polycrystalline thin-film cells were prepared using vacuum evaporation techniques for both the CdS and CuInSe_2 layers⁽⁶⁻⁸⁾. The CuInSe_2 films used in the cells were formed by codeposition of the CuInSe_2 and Se in order to form controlled resistivity, P-type layers. These cells have shown photocurrents of 28 mA/cm^2 , open circuit voltages of 0.49V, and efficiencies of 6.6% when tested with a light intensity of 100 mW/cm^2 . The cells have been approximately 1 cm^2 in area and have not been coated with any anti-reflection layers.

As established in a previous study, the elemental evaporation process for the selenide film formation is believed to possess a number of favorable features, including semiconductor film quality and suitability for scale up to high volume production⁽²⁾. It is the approach Boeing has taken to further the development of this attractive thin-film solar cell. By utilizing these films to fabricate solar cell devices, a cell efficiency of 5.7% has been achieved. Cell performance of this magnitude is viewed as being very encouraging and is also felt to provide an indication regarding the future potential of the planned technical approach.

3.0 TECHNICAL DISCUSSION

3.1 CuInSe₂ Film Deposition

The ternary material CuInSe₂ for this thin-film solar cell program is prepared by a simultaneous elemental evaporation technique onto a heated substrate. As shown in previous programs, this method is capable of producing photovoltaic quality, single phase chalcopyrite CuInSe₂^(1,2). While either N-type or P-type semiconducting thin films could be obtained, the effort has concentrated only on the P-type variety in context with the planned heterojunction cell involving N-CdS. Some properties of these one micron thick films deposited at 475°C onto alumina substrates were: hole mobilities of 9.2 cm²/V-sec; resistivities of 14.8 ohm-cm; carrier concentrations of 4.6×10^{16} cm⁻³; and grain sizes of approximately one micron.

In the earlier work, it was found that the electrical properties of the CuInSe₂ film material were extremely sensitive to the Cu:In ratio. Variations of a few percent in this ratio resulted, for example, in resistivity gradients of 10^4 to 10^5 across the 2" x 2" substrate. With separated Cu and In vapor sources, it was not possible to sufficiently lower these composition variations to a point where uniform films of 1 cm² in area could be achieved. The problem was overcome by utilizing a heated baffle box to mix the Cu and In vapors before they are impinged onto the substrate. A schematic of the deposition equipment is depicted in Figure 3.1.

Although CuInSe₂ films of good uniformity and properties (as described previously) were obtained, the system reliability and deposition reproducibility were very poor. For example, deposition runs frequently had to be aborted due to a failure of one of the three quartz crystal monitors or a vapor source/baffle box failure. Nonreproducibility in the film depositions was attributed to sensor arrangement for Cu and In. That is, to achieve separation of the two vapors for monitoring purposes while close coupling of the source crucibles to the heated baffle box, small holes were made in each end of the box. Consequently, the monitoring beams were more indicative of the vapor entering the box than of the exiting vapor make up which was directed to the substrate.

FIGURE 3.1-1 Schematic Drawing of Vapor Homogenization Deposition Apparatus for CuInSe_2 Films

As there did not appear to be an effective means for significantly improving the control conditions, alternative deposition monitoring approaches were reviewed and evaluated for the present application.

A dual channel co-evaporation controller (Inficon Model Sentinel 200) based upon electron impact emission spectroscopy (EIES) was selected as being the most appropriate. With the EIES technique, evaporant enters a miniature sensor structure and is cross-bombarded by a low energy electron beam. A fraction of the atoms are excited during the collision process. In the excited state, the outer shell electrons of these atoms are raised to energy levels higher than the normal ground state. Almost immediately, most of the excited atoms cascade to lower energy states, emitting photons with specific energies or wavelengths. These wavelengths are generally in the 2000Å to 4500Å ultraviolet light region and are precisely characteristic of the atomic species. The number of photons emitted (light intensity) is proportional to evaporant density in the sensor so that light intensity is then proportional to evaporation rate. By the use of narrow band pass optical filters and/or monochrometers, two specific materials can be simultaneously monitored and rate controlled.

An EIES controller was acquired for the program equipped with an optical filter on one channel and a monochromator on the other. Because of an overlap of the major Cu and In emission lines, i.e., Cu-3247Å and 3274Å and In-3256Å, a band pass filter was incorporated for monitoring the In 4511Å line and the monochromator was set to transmit a minor Cu emission line at 2182Å. The sensor was mounted on the chamber bell-jar and positioned above but off-axis from the baffle-box exit port. Upon experimenting with the instrument, a number of serious deficiencies were revealed. Foremost was a low signal strength for the evaporating copper material. Contributing to the low signal were the low vapor throughput of the baffle box, the necessity of using a minor Cu emission line, the monochromator losses, and the necessity of using a very narrow slit in front of the monochromator to block adjacent In lines. In addition to the low signal for monitoring and control, the very slow response of the vapor source-baffle box system prevented maintaining a constant evaporation rate at a desired value for any length of time. A further problem area relating to the heated vapor mixing approach was the high thermal loading and resulting outgassing due to the large, high temperature, baffle box. The EIES controller was found to be sensitive to the chamber pressure variations which adversely affected the control of Cu and In rates.

In view of all of these factors, it was decided that it would not be possible to combine the EIES controller and baffle-box source structure such that the necessary improvement in deposition reproducibility could be achieved. The development of alternative source configurations which would be compatible with the EIES controller was then initiated.

A successful source design which evolved from this study is shown in Figure 3.1-2. The key feature is a crossed boat configuration for the Cu and In vaporization. Both boats are made of tungsten, contain an alumina barrier, and were obtained from R.D. Mathis Company, Long Beach, California. The boat widths are 1/2" and 3/4" for Cu and In, respectively. A carbon block was inserted in the center of the In boat in order to maintain two vapor sources on each side of the Cu. Finally, spacing between the boats was approximately 1/8". The EIES sensor was located so that it could 'see' both of the In sources as well as the central Cu boat.

With the above configuration, it was impossible to retain the original ring source for the Se evaporation. Instead, two boats were installed on opposite ends of the substrate for deposition uniformity. Selenium vaporization rate was controlled with a quartz crystal deposition controller and shields were incorporated to avoid directly exposing the EIES sensor to Se. While the sensor would still function in the presence of Se, there was the possibility of this high vapor pressure material being transported through the attached light pipe, coating the feedthru window, and thereby attenuating the Cu and In optical signals.

After resolving a series of electronic failures in the EIES unit, the described deposition apparatus and controllers were found to be quite reliable and reproducible within the limits of the EIES controller itself ($\approx 3-5\%$). Although tighter control would be desirable for this extremely composition sensitive material system, it is believed that the present configuration will be sufficient to accomplish the program objectives.

Selenide films were deposited with the equipment onto polycrystalline, 2" x 2" alumina substrates heated to 450°C and briefly analyzed. Based upon previous experience, the relative elemental evaporation rates were adjusted to produce

FIGURE 3.1-2 System Configuration for Preparing CuInSe_2 Films Using EIES Deposition Controller

P-type films of $5\text{K}\Omega/\square$ to $800\text{K}\Omega/\square$ sheet resistivity for 2 micron thickness at a deposition rate of $40\text{\AA}/\text{sec}$. Sheet resistivity as a function of substrate position indicated good uniformity ($\pm 10\%$ for low resistivities and a factor of 2-3 for high resistivities) had been achieved. According to reflection and transmission electron diffraction, the deposits were single phase, chalcopyrite CuInSe_2 . SEM analysis revealed, however, a smaller grain size than in the previous films, e.g., they were slightly under one micron in dimension. One possible explanation for the smaller size is the fact that the film deposition rate has been more than doubled, i.e., $40\text{\AA}/\text{sec}$. vs. $15\text{\AA}/\text{sec}$. in order to obtain a stronger signal for the EIES controller. As a reduction in the polycrystalline selenide film grain size will likely degrade cell response, efforts will be made in the future to reverse this trend by increasing the substrate temperature, decreasing the deposition rate, and altering the film composition.

The developed vapor source structure and EIES control method were found to be well suited for the program task directed towards minimizing the amount of expensive and rare In contained in the thin-film cell. For example, all three vaporizing elements were completely independent of one another and the relative evaporation rates (film composition) could easily be adjusted during a selenide deposit simply by reprogramming the applicable controller. In practice, only In evaporation rate has been varied while the Cu and Se rates have remained fixed at values producing the desired resistivity CuInSe_2 .

One micron thickness In deficient films have been deposited onto metallized alumina substrates heated at 450°C . The In evaporation rates were 50%, 80%, and 90% of the final, high resistivity film value. All of these deposits gave P-type behavior according to a hot probe and were low resistivity, e.g., $300\text{K}\Omega/\square$ to $5\text{K}\Omega/\square$.

While the above approach would be successful in terms of reducing In content, forming an ohmic contact to the final CuInSe_2 layer, and generating a back-surface field condition, they all possessed the undesirable feature of nodular growth. The nodules, which were several microns in size, increased in density with In deficiency. Previous experience has shown such nodules to greatly degrade the cell performance. Whether they can be prevented by depositing the In deficient layer at a lower substrate temperature is not yet known but will be explored in the course of additional research.

3.2 Chemical Analysis of CuInSe₂ Thin Films

In order to characterize the elemental compositions of the selenide thin films, we have made EDAX (Energy Dispersive Analysis of X-rays) measurements on an electron microprobe machine (Applied Research Labs, Model SEMQ). An electron beam of 30kV and 0.1 μ A is focused to a spot of 0.1 μ m and directed normal to the sample surface in a vacuum of 5×10^{-6} torr. The primary beam is made to scan a chosen area of 25 μ m x 25 μ m. The x-rays emitted from the sample (up to a depth of 5 μ m and at a take-off angle of 52.5° to the surface) are detected by a lithium-drifted silicon detector. The signals are pulse-height analyzed and stored in a multi-channel analyzer. The results of accumulated counts (after 100 sec. at 1 scan/sec.) versus channel number (1000 channels at 20eV per channel) can be displayed on an oscilloscope, plotted on an x-y recorder, or further processed on a microcomputer. A typical EDAX spectrum of a CuInSe₂ solar cell sample is shown in Figure 3.2-1.

The x-ray fluorescence lines are readily identified as those from elemental Cu, In, and Se. Any impurities, if present at more than 0.01% by weight, would have been detected. The EDAX method yields quantitative information about the elemental compositions which is reproducible to about $\pm 1\%$. However, the spectral resolving power is limited to about 200eV so that the chemical shifts of the x-ray lines (usually about 1 to 10eV) cannot be detected.

The x-ray spectrum can be processed by the computer to correct for the atomic number, the self-absorption, the fluorescence yield, and the background. If we assume that the intensity of a given x-ray line is directly proportional to its concentration in the sample, then the weight percentage (wt. %) can be computed. Since we are mainly concerned with film compositions nearly stoichiometric to CuInSe₂, the difference between samples in ionization cross section, backscattering factor, and density would be small. In Table 3.2-1, we summarize the measured and computed wt. % for two Boeing samples prepared by the co-evaporation method, as well as a standard sample from Prof. J. J. Loferski's group of Brown University. The Cu K α_1 , Se K α_1 , and In L α_1 were used in the data processing for wt. % values. From the data in Table 3.2-1, we see that each sample exhibits a fairly uniform composition as a function of position. Whereas the Boeing samples definitely contain more In, the Brown sample seems to be richer in Cu and Se. Our next step will be to

FIGURE 3.2-1 EDAX Spectrum of CuInSe_2 Thin Film Prepared by Simultaneous Elemental Evaporation

TABLE 3.2-1 SUMMARY OF EDAX RESULTS ON CuInSe₂ THIN FILMS**Boeing
Sample #128
(low
resistivity-
8K Ω /)

Distance (cm)	0.5	1.5	2.5	3.5	4.5	Average
In (%)	37.50	38.02	37.75	37.62	37.86	37.75
Cu (%)	17.96	17.71	17.83	18.08	17.56	17.83
Se (%)	44.54	44.27	44.42	44.30	44.58	55.53

Boeing
Sample #130
(high resis-
tivity -
>10⁶ Ω /)

Distance (cm)	0.5	1.5	2.5	3.5	4.5	Average
In (%)	38.68	38.88	38.48	39.50	39.25	38.96
Cu (%)	16.67	16.73	16.93	16.30	16.45	16.61
Se (%)	44.65	44.39	44.59	44.20	44.30	44.43

Brown Univ.
Sample

Position	Center	Four Spots at 2mm From Center				Center	Average
In (%)	35.98	35.22	36.67	36.51	36.60	35.85	36.14
Cu (%)	18.13	18.51	18.15	18.30	18.02	18.02	18.19
Se (%)	45.89	46.27	45.18	45.19	45.38	46.13	45.67

**Theoretically, the wt. % for a perfectly stoichiometric CuInSe₂ sample should be
In = 34.14, Cu = 18.90, and Se = 46.96.

try to establish a connection between the composition and the solar cell performance. The possibility of using other analytical techniques for thin film characterization will also be explored.

3.3 Development of Low Cost Cell Metallizations

The CdS/CuInSe₂ thin-film cells developed in the earlier program utilized a sputtered Mo/Au metallization. The thin Au layer (500-1000Å) was intended to serve mainly as an ohmic contact to the selenide film. Even for this thickness, the gold would be too costly in future large scale cell production. Accordingly, several inexpensive metallizations which can be prepared by low cost manufacturing methods have been investigated as potential replacements for the gold layer.

Since the low resistivity, P-type, In deficient layer would be deposited as an interface between the metallization and the CuInSe₂ film, achieving an ohmic contact to the selenide with the different metal systems was not a major factor in the candidate metal selection. Instead, the criteria were: relative abundance and cost; high electrical conductivity, stability (chemical, thermal, and environmental) and amenability to vacuum, sputtering, or plating deposition processing.

The first series of metallizations examined were based upon copper. They included Cr/Cu, Zn/Cu, and brass deposited by vacuum evaporation or RF sputtering only polycrystalline alumina. After depositing a selenide film at 450°C onto these metallizations, it became apparent that the Cu rapidly diffused through and altered the selenide properties. Consequently, Cu based metallizations have been rejected for this program which requires very high selenide film deposition temperatures.

Vacuum deposited nickel films were also rejected because of a reaction with the selenide material which lead to a peeling of the film composites from the substrate.

Finally, vacuum evaporated molybdenum film were evaluated and found quite acceptable with regards to stability, adhesion, and ohmic selenide film contact. However, films even as thick as two microns displayed rather high resistivities of $1\Omega/\square$. RF sputtered films were next prepared and exhibited low resistivities

of $0.2\Omega/\square$ for films of $3000\text{\AA}$ in thickness. These films were sputtered in 6 microns of argon with a power of $13.5\text{W}/\text{in}^2$ for 20 minutes. At the present time, all of the sputtered Mo film properties are believed to be consistent with the goals of the low cost metallization development task and this metallization will be applied in future cell research studies.

3.4 CdS Film Preparation

Along with the described revisions to the selenide vaporization apparatus, the CdS source has been modified from that used earlier. The original source was composed of a fused quartz crucible container for the CdS powder, a flat spiral radiant heater, and quartz wool baffling. Since it was difficult to consistently pack the quartz wool to the same density to prevent particulate emission, a more repeatable source was developed. This new source is a partitioned tantalum foil box with a reusable quartz wool pad in the center or vapor emitting chamber. The CdS films prepared with the box evaporator were similar in electrical properties to the earlier films but deposited particulate material was less of a problem. At a 150°C deposition temperature, the sheet resistivity for 3-5 micron thick films was in the range of $60\text{--}200\text{K}\Omega/\square$. For CdS films actually deposited in cells, the outermost layer will again be doped with In ($\approx 1.5\%$) to produce a very low resistivity ($30\text{--}100\Omega/\square$) region in contact with a deposited grid structure. This In doping will be accomplished by a co-evaporation technique of elemental In and CdS.

3.5 CdS/CuInSe₂ Cell Development

Cell Structure Design

The basic CdS/CuInSe₂ cell structure has been redesigned to accommodate several concepts for cell improvement, i.e., low cost metallized substrate, minimizing In content, and composition gradients. One possible structure is schematically shown in Figure 3.5-1.

The In deficient CuInSe₂ is a strongly p-type, low resistance material. The introduction of this layer in the cell structure would have three main purposes:

- (1) Reduces the difficulty in making a low resistance ohmic contact to metals other than the expensive Au;

FIGURE 3.5-1 Redesigned CdS/CuInSe₂ Cell Structure

- (2) Creates a backside field to improve the cell efficiency; and
- (3) The thickness of the active CuInSe₂ layer could be reduced to minimize the cell In content.

After the In deficient selenide deposit, the In content in the vapor stream would be gradually increased to a value which would form CuInSe₂ of the proper resistivity to make a good heterojunction with CdS. This structure could also be used in a future study on the effect of a doping gradient (built-in field) in the CuInSe₂ layer by changing the stoichiometry.

The in-situ deposited CdS would also have two layers. The CdS layer adjacent to the heterojunction would be deposited without In doping to avoid the In-contamination of the heterojunction. The outer layer of low resistivity In doped CdS would be beneficial in lowering the cell series resistance. An aluminum grid would then be deposited onto the doped CdS surface to complete the cell (excluding an antireflection coating).

Theoretical Analysis

During this quarter, work has been concentrated on analyzing the model introduced by Kazmerski, et. al.^(9,10) They assume that the cell is dominated by interface recombination and the cell characteristics are given by:

$$J = J_0(e^{\frac{V}{nKT}} - 1) - J_L$$

$$\text{and } J_0 = qN_C S_I e^{\frac{E_g - \Delta x}{nKT}}$$

where E_g = the bandgap energy of the CuInSe₂

N_C = effective density of states of the CdS conduction band

S_I = interface recombination velocity

Δx = electron affinity difference between CuInSe₂ and CdS

n = diode factor

From their V_{oc} and J_0 versus temperature measurements (Figure 2 and Figure 3 in Reference 9), they determined $\Delta x = 0.08\text{eV}$ and $N_C S_I = 5 \times 10^{24} \text{ cm}^{-1}\text{sec}^{-1}$ or $S_I = 2.4 \times 10^6 \text{ cm/sec}$ ⁽¹⁰⁾ which is in very good agreement with the calculated value based upon the lattice mismatch of the two semiconductor materials.

However, upon closer examination of their J_0 vs. temperature results (Figure 3 Reference 9), where J_0 (A/cm^2) is plotted against $(nkT)^{-1}$. J_0 is shown to be approximately $2 \times 10^{-2} \text{ A/cm}^2$ at room temperature [$(nkT)^{-1} = 18.4\text{eV}^{-1}$, for $n = 2.1^{(11)}$] which is four orders higher than the value they reported elsewhere (Figure 2 in Reference 11). This inconsistency may be from mislabelling the units of either the abscissa and/or ordinate (Figure 3 Reference 9). In either case, the value of N_{CSI} will be in error by 4 orders from the calculated value or $E_g - \Delta X$ (from the slope of Figure 3 Reference 9) will be 1.9eV [if plotted against $(kT)^{-1}$ instead of $(nkT)^{-1}$].

A more detailed analysis and extension of their model has been somewhat hindered by this apparent discrepancy. During next quarter, it is anticipated that the discrepancy will be resolved by coordinating with Kazmerski's group to interpret the recombination mechanism.

3.6 Stability of CdS/CuInSe₂ Cell

While an important future task will involve a determination of the stability of thin-film CdS/CuInSe₂ cells through a rigorous life test program, at present there are insufficient quantities of high efficiency cells to begin such an examination. The relative stability of the few existing cells is, however, believed to be of considerable significance. It has been observed, for example, that in the case of Boeing's highest efficiency (5.7%) thin-film CdS/CuInSe₂ cell when remeasured after nearly eight months there has been no measurable degradation in photoresponse. This cell, which was not passivated or otherwise protected, has been stored simply in the normal laboratory environment. No attempt has been made to protect the device (except from mechanical or electrical abuse) by storage in a hermetic or dry nitrogen purged atmosphere. It has periodically been tested under simulated sunlight and then returned to the open sample case for storage under ambient lighting levels. The dark and light I-V curves for the cell soon after its fabrication and after eight months storage are shown in Figure 3.6-1. The light curves were made using simulated sunlight from a tungsten-halogen lamp set for 100mW/cm^2 intensity with a standard silicon cell. Within experimental error, no detectable change in the cell properties had occurred during the storage time span. This apparent stability of a completely unprotected device in such an environment is believed very encouraging and suggests that cell degradation will not be a limiting problem with the CdS/CuInSe₂ thin-film cell.

A. On September 29, 1978

B. On June 15, 1979

FIGURE 3.6-1 Light and Dark I-V Characteristics of Boeing's Highest Efficiency CdS/CuInSe₂ Thin Film Cell. Simulated Sunlight at 100mW/cm².

4.0 PLAN FOR NEXT QUARTER

During the next quarter (June 1, 1979 - August 31, 1979), the program plan includes the following:

- 1) Deposition and characterization of In deficient CuInSe_2 films deposited at substrate temperatures lower than 450°C .
- 2) Fabrication and analysis of CdS/CuInSe_2 heterojunction test structures incorporating advanced cell design concepts.
- 3) Application of experimental cell data to the development of the cell conceptual model.

5.0 REFERENCES

1. R. A. Mickelsen and W. S. Chen, "Improved Semiconductors for Photovoltaic Solar Cells - CuInSe₂", Final Report, Contract E(49-18)-2459, August 1977.
2. R. A. Mickelsen, W. S. Chen, and B. Selikson, "Cadmium Sulfide/Copper Ternary Heterojunction Cell Research", Final Report, Contract EG-77-C-03-1458, October 1978.
3. S. Wagner, et. al., Appl. Phys. Lett. 25, 434 (1974).
4. J. L. Shay, et. al., Proc. Eleventh Photovoltaic Specialists Conf., Phoenix, Arizona, p. 503 (1975).
5. S. Wagner, et. al., Appl. Phys. Lett. 26, 229 (1975).
6. L. L. Kazmerski, "Ternary Compound Thin Film Solar Cells", Final Report, NSF/RANN/SE/AER 75-19576/PR/75/4, October 1976.
7. L. L. Kazmerski, et. al., Appl. Phys. Lett. 29, 269 (1976).
8. L. L. Kazmerski, et. al., J. Vac. Sci. Technol. 14, 65 (1977).
9. L. L. Kazmerski, et. al., Proc. Thirteenth Photovoltaic Spec. Conf., Washington, D.C., p. 184 (1978).
10. L. L. Kazmerski, Solid State Electronics 21, 1545 (1978).
11. L. L. Kazmerski, Ternary Compounds 1977, Instit. Phys. Conf. Series, No. 35, p. 217 (1977).