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MASTER

CADMIUM SULFIDE/COPPER SELENIDE CELL RESEARCH

COPPER SELENIDE-BASED THIN FILM SOLAR CELLS

(XG-Ø-9216-1)

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Abstract

The objective of this program is to investigate the use of $Cu_{2-x}Se$ to produce low cost, high efficiency photovoltaic solar cells. This program is the first phase of an effort leading to the development of low cost thin film arrays. The goal is to: (1) develop a polycrystalline thin film photovoltaic device capable of 10% conversion efficiency, (2) demonstrate feasibility of large scale production at a cost of approximately $0.30/watt.

The $Cu_{2-x}Se$ films are produced by coevaporation of Cu and Se from separate, individually controlled vapor sources onto heated glass substrates. This method gives greater composition controllability and is readily adaptable to large scale production efforts. Two quartz crystal microbalances are used to separately monitor the Cu and Se deposition rates.

The structural, electrical, and optical properties of the $Cu_{2-x}Se$ films have been measured for deposits made on 250°C substrates. The optical absorption measurements shows the material having an indirect band gap of 1.4 ev and a direct gap of 2.2 ev. These values are for stoichiometric indices in the range of $0.17 \leq x \leq 0.26$. Hall and conductivity measurements give hole mobilities in the range of 3-7 cm^2/Vsec and hole densities of the order of 4×10^{22} cm^{-3}. For deposits made on substrate at 160°C, the mobility is in the range of 3-10 cm^2/Vsec and hole densities on the order of 10^{18} to 10^{21} cm^{-3} for $0.1 \leq x \leq 0.3$.

To date, the best cell has photovoltaic characteristics of J_{sc} = 11.6 mA/cm^2, V_{oc} = 460 mV, F.F. = 0.62 and η = 3.3% when tested under simulated AM1 illumination. In an effort to improve cell performance, low resistance CdS was used. Cell performance degraded considerably with the low resistance CdS resulting in substantially lower values for both V_{oc} and I_{sc}. It is believed in part that this difficulty can be traced to "pinhole" defects in the ITO electrode. When the low resistance CdS is deposited on ITO, regions in the CdS appear to be high in Cd where "pinholes" in the ITO were observed.

1.0 SUMMARY

The major results for the reporting period September 1, 1980 through December 1, 1980 can be summarized as follows:

a. An attachment to the Cary 14 spectrophotometer has been devised so that the photoluminescent spectra of CdS can be measured when the CdS is illuminated by a Hg lamp. This will be of use in the future to assure that the CdS is properly doped.

b. Problems associated with the deposition of low resistance CdS onto ITO coated glass have been investigated. The results show the CdS to be off stoichiometry (Cd rich) in the region where "pinholes" in the ITO appear.

c. The effect of low resistance CdS on device performance has been investigated. In general, the low resistance CdS yields cells of low V_{oc} and I_{sc}.

2.0 INTRODUCTION

This is the second quarterly report of a 12-month research program to investigate the use of $Cu_{2-x}Se$ to produce low cost, high efficiency photovoltaic solar cells. This program is the first phase of an effort leading to the development of low cost thin film arrays. The goal is to: (1) develop a thin film photovoltaic device capable of 10% conversion efficiency, (2) demonstrate feasibility of large scale production at a cost of approximately $0.30/watt.

$Cu_{2-x}Se$ has a number of characteristics that give it excellent potential for yielding a 10% efficient solar cell. Band gap measurement by previous investigators have found values in the range of 1.1 to 1.29 eV.[1,2] Measurements by this laboratory have given values of 1.4 eV for the indirect band gap and 2.2 eV for the direct band gap. The f.c.c. structure obtained has a lattice constant of a = 5.76Å. This will then give a very small lattice mismatch with the N-type CdS layer. With the use of N-type CdS, consideration of the electron affinity of the materials shows there will be no detrimental interfacial spike in the conduction band between the two materials. Hall and conductivity measurements give hole mobilities in the range of 3-10 $cm^2/Vsec$ and hole densities on the order of 10^{18} to 10^{21} cm^{-3} dependent on the stoichiometric index "x". These values are for $Cu_{2-x}Se$ deposited on a glass substrate at 160°C.

Progress in the area of increasing device performance has been slow due to problems encountered in the deposition of low resistance CdS onto ITO coated glass substrates. A variety of defects in CdS can be observed. These defects most likely occur due to "pinholes" in the ITO. Analysis of these defects reveal a substantial increase in the amount of Cd at these sites. It is believed that cell performance is degraded because of this phenomena.

Specific objectives to be attained in the remaining period of this contract are: 1) perform theoretical and experimental modeling of the $Cu_{2-x}Se$/CdS heterojunction, making detailed measurements so that the mechanisms that limit conversion efficiency of the cell can be determined; 2) produce a 4% efficient cell by the end of the third quarter and a 6% efficient cell by the end of the contract.

3.0 TECHNICAL DISCUSSION

3.1 Film Characterization

3.1.1 Characterization of $Cu_{2-x}Se$

The electrical properties of $Cu_{2-x}Se$ deposited onto a glass substrate at $160^{o}C$ have been measured. A plot of stoichiometric index "x" versus resistivity shows a high resistance rear x approximately 0.1 (Figure 3.1). One would expect the resistance to be a maximum near x = 0, however, we have observed some Cu nodule formation in the range $0 \leq x \leq 0.1$. While the best match of the $Cu_{2-x}Se$ lattice to the CdS lattice occur for x approximately 0.2, there are indications that the total device performance may be higher near x equal to 0.1. The value of the stoichiometric index x was determined by coulometric techniques.[3]

The carrier concentration was determined by the Van der Panw technique.[4] The carrier concentration was approximately 10^{20} holes/cm^3 for all values of x except near x equal to 0.1. At this value of x the carrier concentration dropped to 10^{18} holes/cm^3. The mobility was approximately 10 cm^2/Vsec.

SEM studies of $Cu_{2-x}Se$ deposited on low temperature ($\leq 160^{o}C$) glass substrates reveal a porous film structure (Figure 3.2). More study is necessary to determine why a poorly defined grain structure resulted at this temperature. Deposits of $Cu_{2-x}Se$ onto high temperature substrates show good grain definition and a dense, compact film structure.

3.1.2 Characterization of CdS

An attachment for the Carry 14 spectrometer to make photoluminescent measurements has been designed and built. This will serve as a valuable evaluator of CdS films in assuring that the films exhibit the proper photoluminescent spectra.[5] This measurement has a particular advantage in that it probes the top 100 nm of the film in comparison to resistivity measurements made through the film.

The grain boundaries in the CdS are revealed by the following procedure. Cu_2S is first formed on the surface of the CdS using a CuCl solution. The Cu_2S is then stripped from the surface with KCN.[6] The Cu_2S forms preferentially in the grain boundaries of the CdS and results in readily visible crevices at the boundaries. Measurements of grain size are then made by use of the SEM at normal incidence. SEM results of low (~ 1 ohm-cm) and high (> 100 ohm-cm) resistance CdS are shown in Figure 3.3.

Many problems have occured in trying to make good quality, low resistance CdS films on ITO coated glass. The main difficulty is that the low resistance CdS appears to exhibit sites of nonuniform growth where "pinhole" defects appear in the ITO. The defects in the CdS were examined by a scanning electron microprobe quantometer. The defects described above show a significant increase in Cd compared to the more uniform portions of the film. An example of such a defect is shown in Figure 3.4 where a microprobe scan across the film surface shows a significant increase in the Cd concentration.

After a CuCl/KCN etch procedure, a SEM analysis of the CdS surface shows only slight variation in the grain size, whether the CdS is deposited directly onto the glass substrate or onto ITO coated glass (Figure 3.5).

3.2 Cell Construction

Cell fabrication is accomplished in much the same manner as in the previous quarter. Changes were made in the layout of the film on the substrate so that the contact resistance between the electrodes and film could be measured, and additionally the film sheet resistance and transverse resistance can be determined.

A schematic of the various steps in construction of a backwall cell is shown in Figure 3.6. First a Mo/Au grid is formed by a combination of sputtering and photoresist-etch techniques (Figure 3.6a). An ITO film is then sputtered over the Mo/Au grid to a thickness of 1000Å and a sheet resistivity of 7 Ω/□ (Figure 3.6b). The CdS film is deposited next to a thickness of 11 μm (Figure 3.6c). The CdS is then etched in 10% HCl at room temperature for 1 minute. The $Cu_{2-x}Se$ film is then evaporated onto the CdS at a substrate temperature of 160°C (Figure 3.6d). Finally an Au electrode is placed on top of the $Cu_{2-x}Se$ film (Figure 3.6e). A cross section of the backwall cell structure appears in Figure 3.7.

3.3 Cell Analysis

At the end of this quarter, the highest cell efficiency is in the neighborhood of 3.3%. This was accomplished by depositing $Cu_{2-x}Se$ onto high resistivity CdS. Typical cell performances after a few minutes heat treatment at 200°C in air (under simulated AM1 illumination) are listed below:

$$V_{oc} = 0.4 - 0.5 \text{ volt}$$
$$I_{sc} = 10 - 12 \text{ mA/cm}^2$$
$$F.F. = 0.5 - 0.62$$

A typical cell made in this quarter is shown in Figure 3.8. A cross over of dark and light I-V curves have been observed in these cells when measured under 60 Hz sweep. However, the dark I-V curves are not stable and drift with time toward a curve characteristic of no cross over when measured under a slow sweep condition. This phenomena is also observed in the Cu_2S/CdS cell.[7] This phenomena has been explained, by the Institute of Energy Conversion group,[7,8] as being due to the Cu-compensated region in CdS exceeding the junction space change region.

In the last quarterly report, a theoretical achievable cell performance has been calculated. An assessment of the performance of the recent cells can probably best be made by comparing their performance with that of the calculated values. Picking I_{sc} ~ 12 mA/cm^2, V_{oc} ~ 0.5 volt, and F.F. ~ 0.62 as being representative of the best cells, the comparison is shown in Table 3.1.

Table 3.1

Comparison of Device Characteristics
To Theoretical Performance

Parameter	Measured*	Theory	Ratio
J_{sc} (mA/cm^2)	12	22	0.55
V_{oc} (V)	0.5	0.63	0.79
F.F.	0.62	0.75	0.83

* Best values observed in different cells.

It is clear that the primary problem with our present cells is the low J_{sc}.

There are several factors that can cause low J_{sc}:

(1) Failure to absorb radiation and produce photocarriers because of the low absorptivity in the $Cu_{2-x}Se$.

(2) Failure of the photocarriers to reach the junction due to the low minority carrier diffusion length in $Cu_{2-x}Se$.

(3) Low collection efficiency because of interface recombination and low junction field.

With our present backwall cell design, the $Cu_{2-x}Se$ thickness is about 3-4 μm. The J_{sc} shows no difference when we put either a gold grid or a solid gold electrode (as light reflector) on the $Cu_{2-x}Se$. This indicates that the $Cu_{2-x}Se$ is thick enough to absorb most the radiation. However, if the minority carrier diffusion length is much shorter than the $Cu_{2-x}Se$ thickness, carriers generated farthe than a few diffusion lengths away from the junction will recombine before they can reach the junction region and be collected.

Reducing the thickness of the $Cu_{2-x}Se$ will force the photo-generated carriers to reside in the region where they can be collected. The unabsorbed radiation through the thin low absorptivity $Cu_{2-x}Se$ layer will be reflected back and be reabsorbed in the $Cu_{2-x}Se$ by use of a light reflecting contact. Hence, by a combination of reducing the $Cu_{2-x}Se$ thickness and using light reflecting contact, it should be possible to increase the J_{sc}.

Another factor affecting the J_{sc} is the interface recombination and the junction field. According to Rothwarf's theory,[9] the field-aided collection efficiency is a function of the interface recombination velocity and the electric field strength at the junction. Within a reasonable range of interface recombination velocity, the collection efficiency can drop from 0.8-0.9 to 0.1-0.3 if the junction field is reduced from 10^5V/cm to 10^3 V/cm. From IEC's experience in developing the Cu_2S/CdS cell, the junction depletion layer width after heat treatment is about 10 μm in the dark and decreases to approximate 0.17 μm under solar illumination.

With a depletion width of 0.17 μm under illumination, the junction field has been estimated as high as 8×10^4 V/cm. The shrinkage of depletion region is caused by trapping of the photogenerated holes by the Cu acceptors in CdS.

The capacitance measurements of our cell indicate that the depletion width extends to about the thickness of the CdS layer (~ 5 μm) after heat treatment. The depletion with shrinks to about 2 μm under illumination. This gives a junction field at least an order of magnitude less than the IEC's Cu_2S/CdS cell. This low junction field may yield a low collection efficiency which degrades the J_{sc}.

According to IEC's findings, certain defect structures in CdS which can be detected by photoluminescence measurements are crucial to producing a good cell. These defect levels may effect the Cu diffusion in the CdS layer and consequently control the junction field.

From a preliminary study of our CdS film, no photoluminescence has been observed. Hence, the quality of our CdS film needs to be improved in order to increase the collection efficiency.

In summary, we propose to examine the role of the $Cu_{2-x}Se$ thickness in ultimately determining J_{sc}. In addition the photoluminescence spectra of CdS will be measured and compared to IEC's results.

4.0 REFERENCES

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3. E. Castel and J. Vedel, Analysis, 3 (1975), 487.

4. H. H. Wieder, Thin Solid Film, 31 (1976), 123-138.

5. R. B. Hall, R. W. Birkmire, E. Eser, T. L. Hench and J. D. Meakin, 14th IEEE Photovoltaic Specialists Conference, San Diego, California, 7-10 Jan 1980, pg. 706-714.

6. B. Baron, A. W. Catalano and E. A. Fagen, 13th IEEE Photovoltaic Specialist Conference, Washington, 1978, p. 406.

7. Institute of Energy Conversion, Progress Report E(49-18)-2538 PR76/1.

8. Institute of Energy Conversion, Final Report E(49-18)-2538 PR77.

9. A. Rothwarf, J. Phillips and N. Convers Wyeth, 13th IEEE Photovoltaic Specialist Conference, Washinton, 1978, p. 399.

5.0 PLAN FOR NEXT QUARTER

The photoluminescent spectra of our CdS will be measured and compared with the spectra measured by IEC. Cell performance will then be correlated with the CdS photoluminescent spectra.

Cell performance will be examined as a function of $Cu_{2-x}Se$ thickness.

In-depth investigation will be conducted to identify the loss mechanisms effecting the photovoltaic performance.

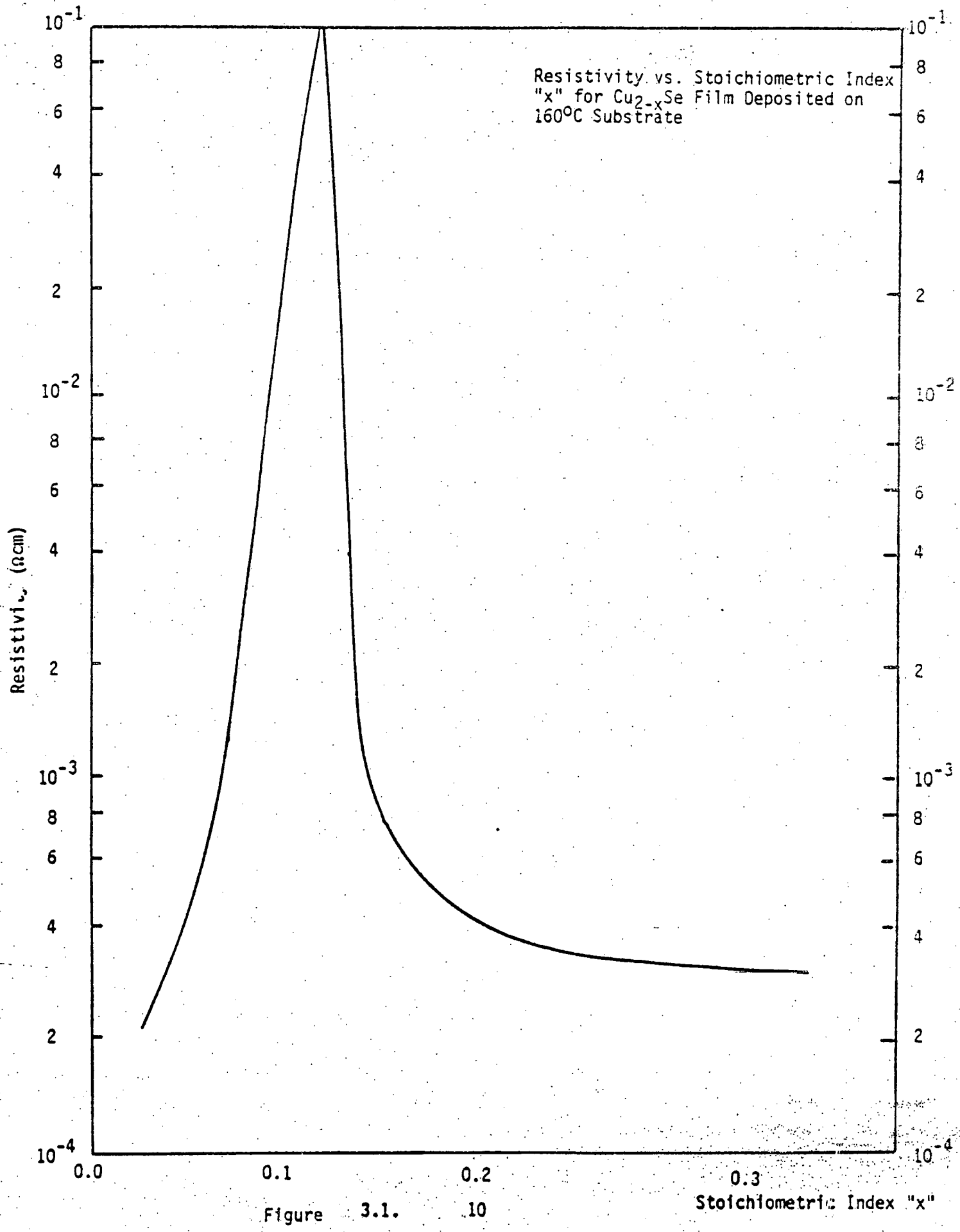
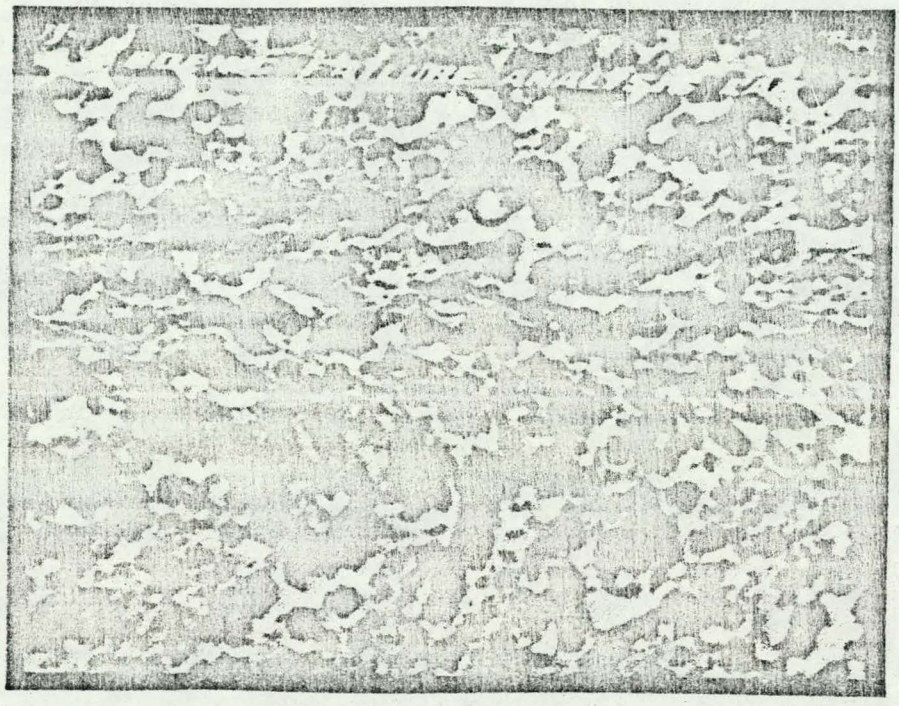
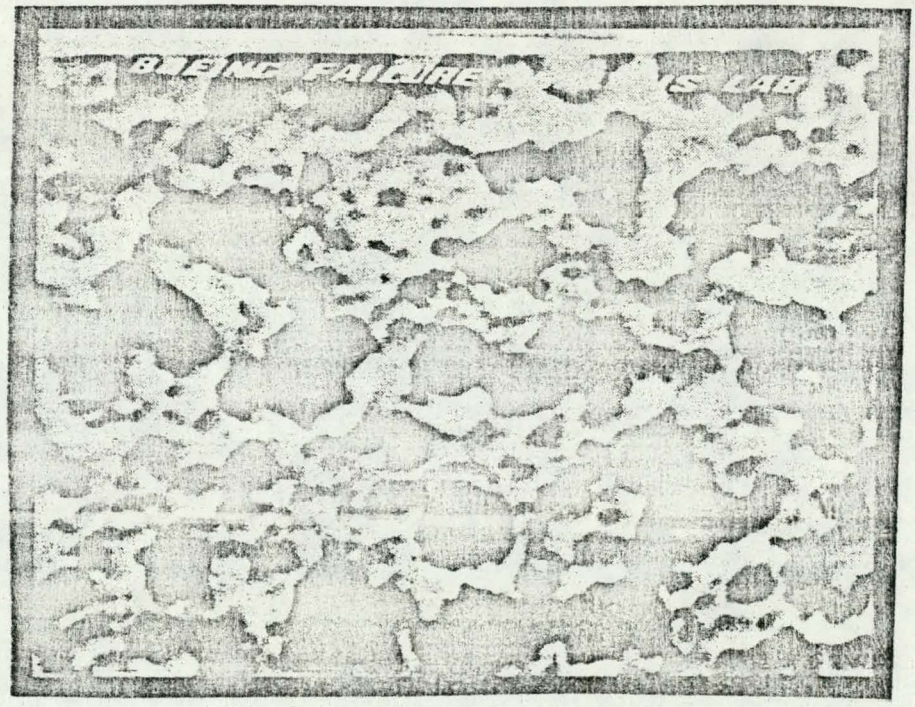

Resistivity vs. Stoichiometric Index "x" for $Cu_{2-x}Se$ Film Deposited on 160°C Substrate
Resistivity (Ωcm)
Stoichiometric Index "x"
10^{-1}
8
6
4
2
10^{-2}
8
6
4
2
10^{-3}
8
6
4
2
10^{-4}
0.0
0.1
0.2
0.3

Figure 3.1.

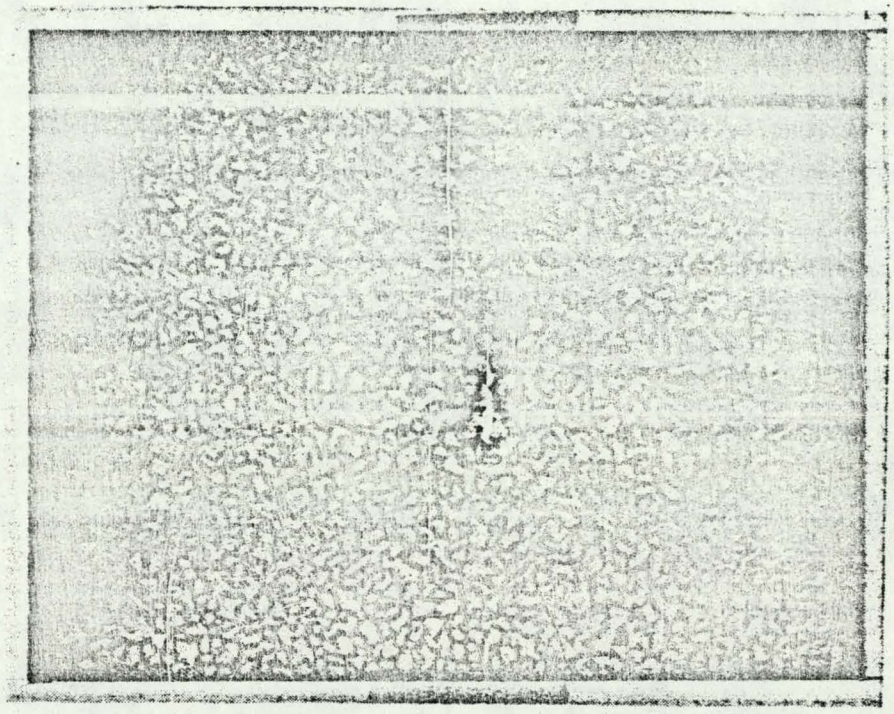


a) 5000X Run #370

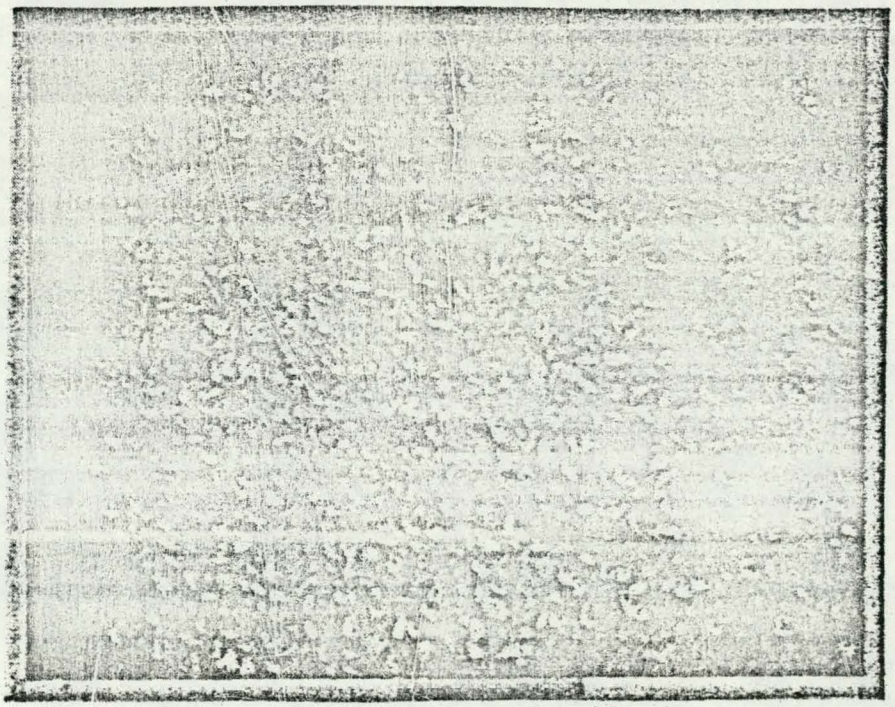


b) 10,000X Run #370

Figure 3.2. SEM Picture of $Cu_{2-x}Se$ at 160°C



a) Low Resistance CdS Run #298 5000X



b) High Resistance CdS 5000X

Figure 3.3. SEM of Low and High Resistance CdS

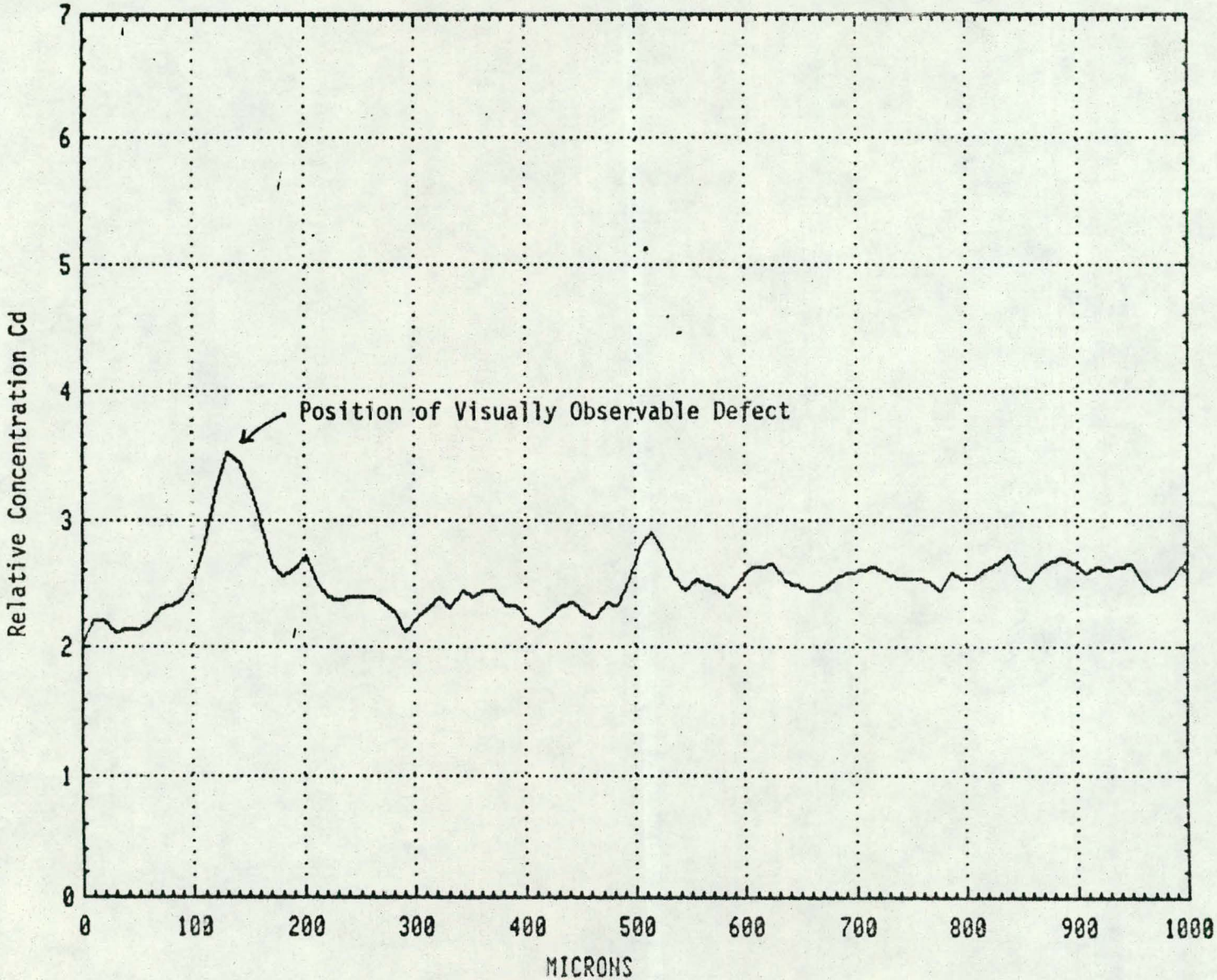
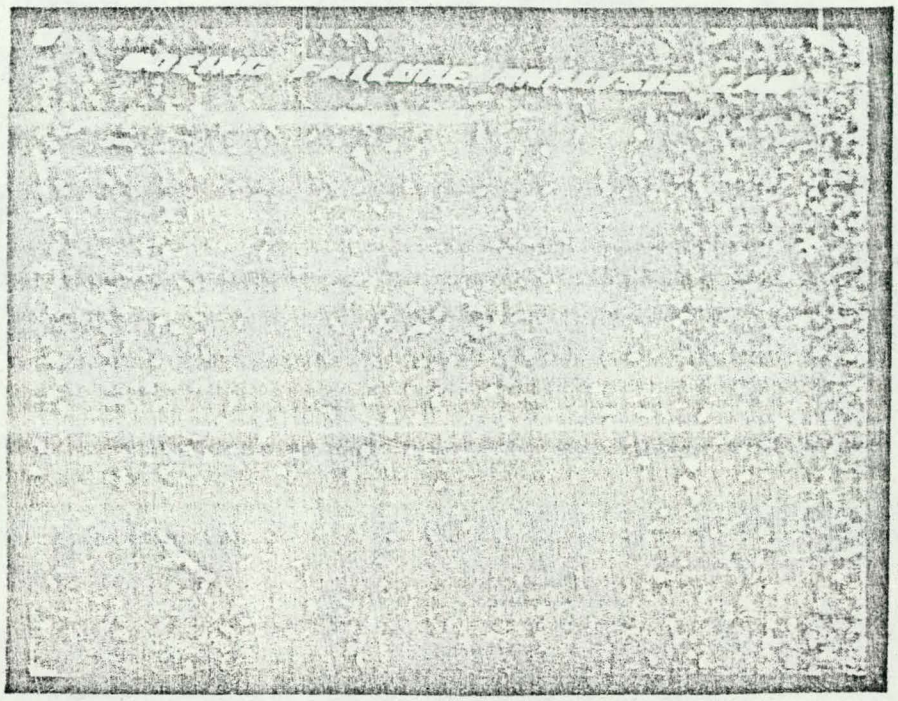
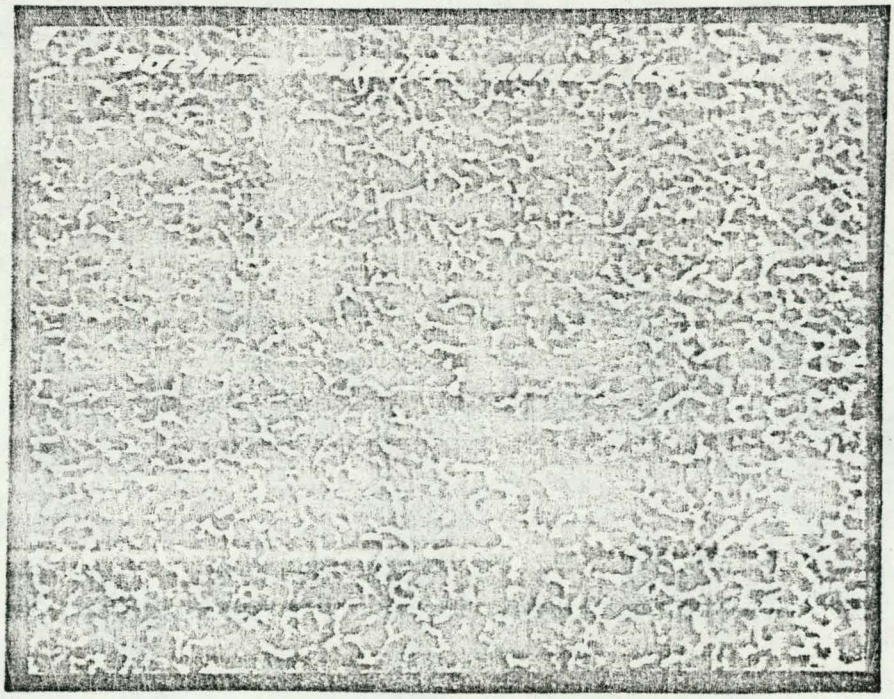


Figure 3.4. Relative Cd Concentration vs Position Across Substrate Showing Cd Increase at Defect Site

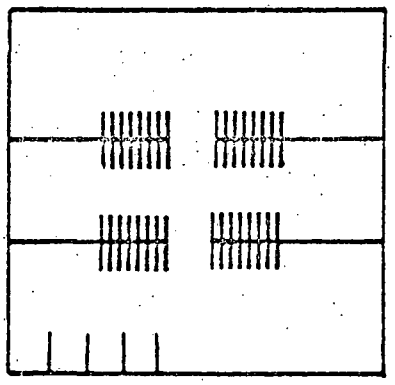


a) CdS on Uncoated Glass 5000X

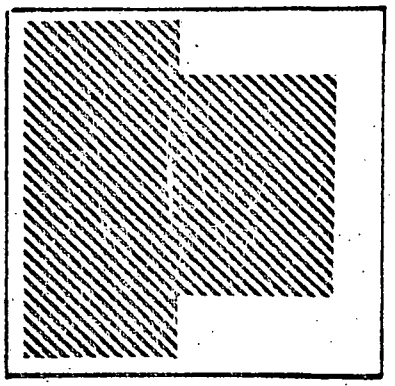


b) CdS on ITO Coated Glass 5000X

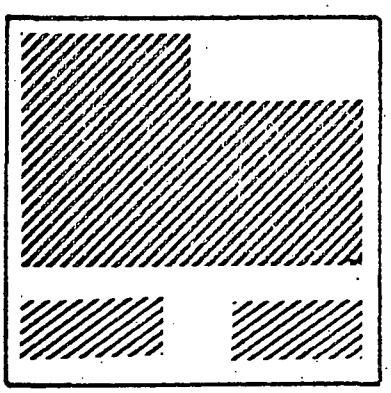
Figure 3.5. Grain Boundaries of CdS on Coated and Uncoated Glass



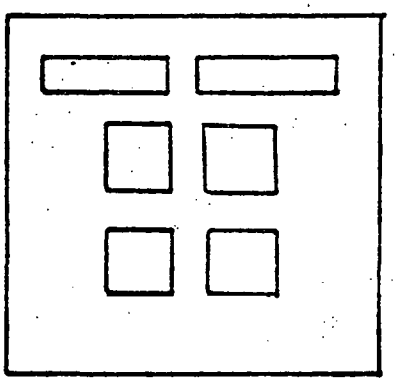
Mo/Au grid plus fingers
to measure contact potential
difference between Au and ITO
(a)



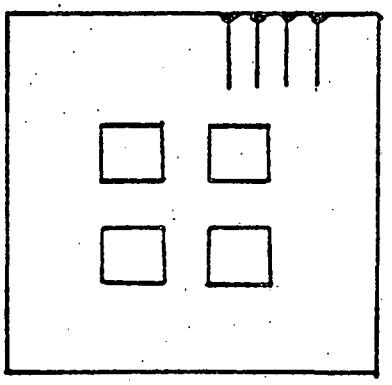
ITO
(b)



CdS for device fabrication, CdS
resistance and coulometry measurement
(c)

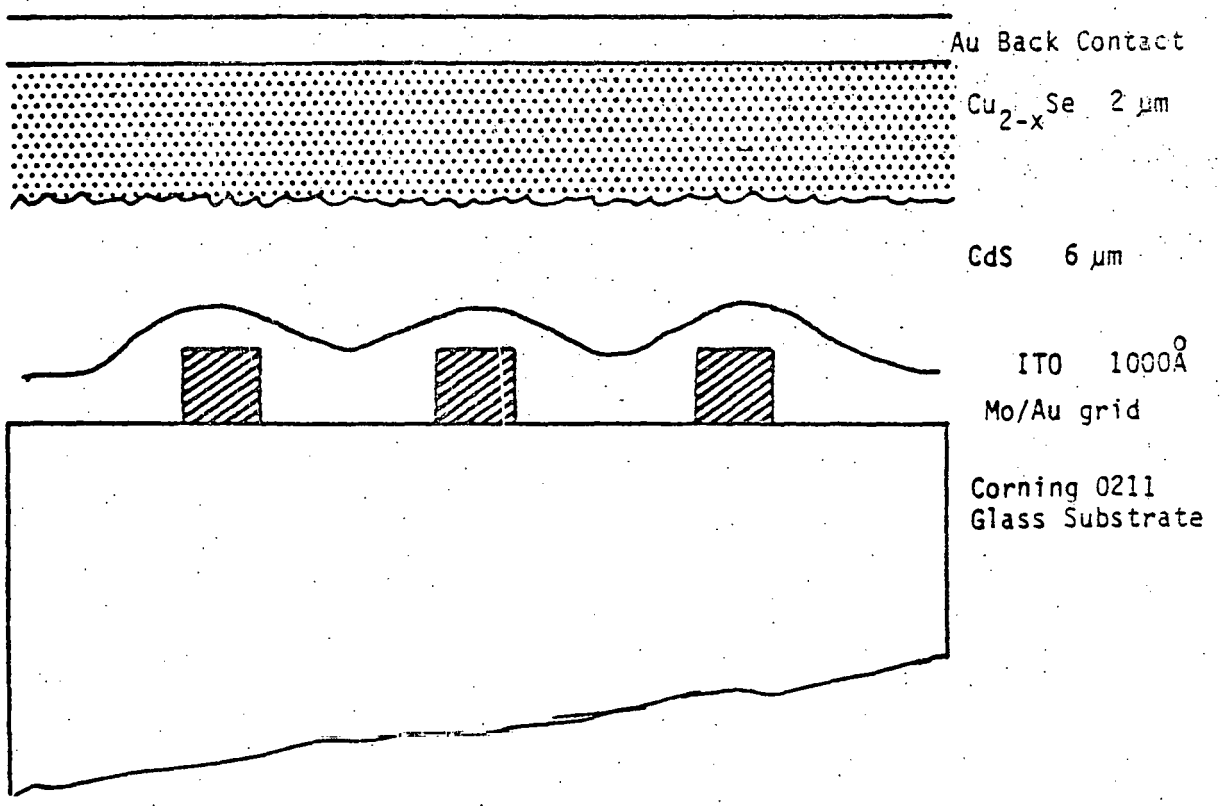


$Cu_{2-x}Se$ for device fabrication
(d)



An electrode for backwall device
plus finger to measure contact
potential between Au and $Cu_{2-x}Se$
(e)

Figure 3.6. Steps in backwall cell fabrication



Back Wall Cell Structure

Figure 3.7

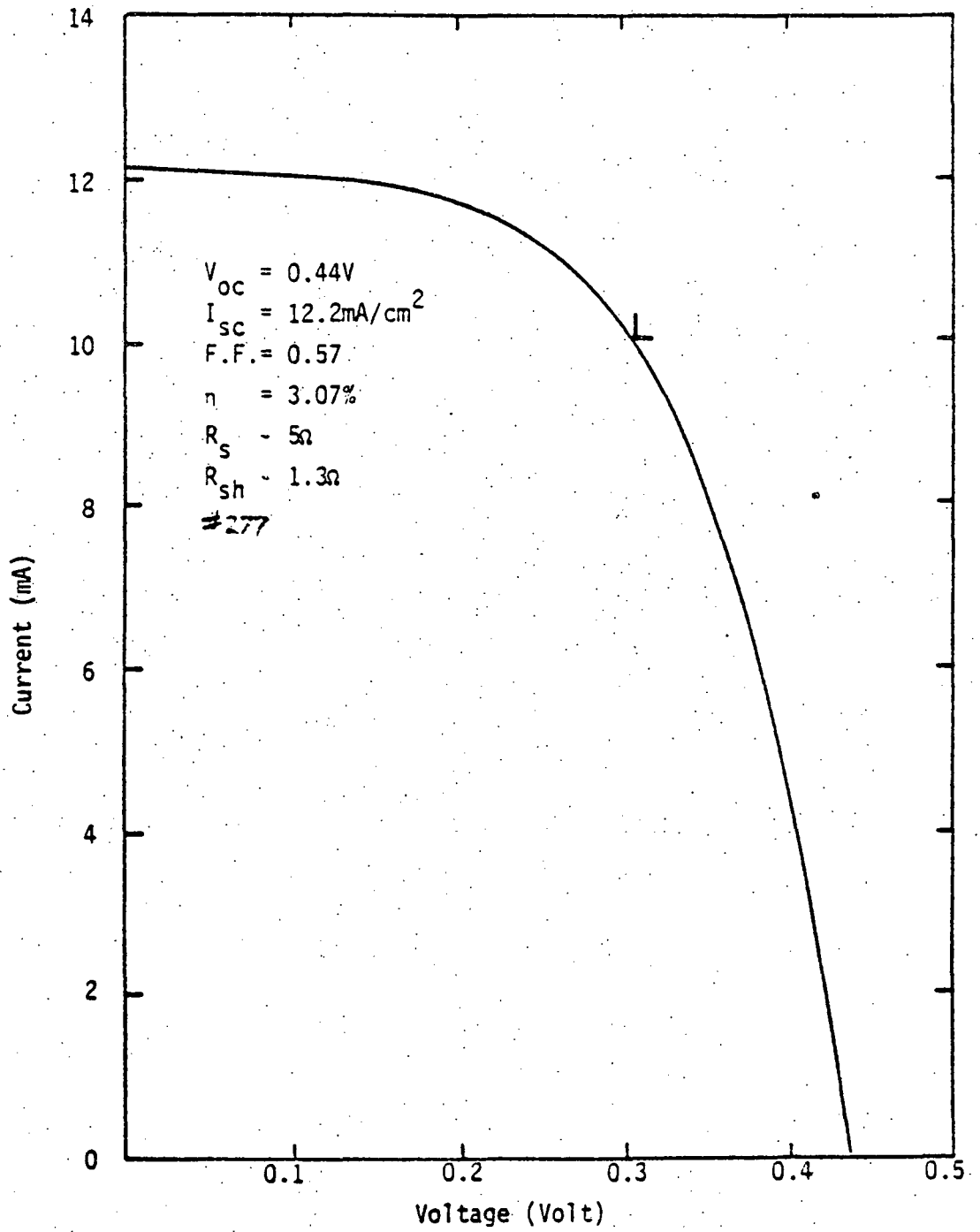


Figure 3-8. Typical Photovoltaic Response of 1cm^2 Cell Under Simulated AM1 Illumination

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