

MASTER

EMERGING MATERIALS SYSTEMS FOR SOLAR

CELL APPLICATIONS - Cu_{2-x}Se

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SECOND QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD

August 1, 1979 - November 1, 1979

R.A. Mickelsen, J.M. Stewart, W.S. Chen
L.F. Buldhaupt - Program Manager

November 1979

Work Performed Under Contract DE-AC04-79ET23005

Boeing Aerospace Company
P.O. Box 3999 M/S 88-43
Seattle, Washington 98124

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
1.0 SUMMARY	2
2.0 INTRODUCTION	3
3.0 TECHNICAL DISCUSSION	4
3.1 Copper Selenide Film Deposition Procedure	4
3.2 Film Structural Studies	4
3.2.1 General Characteristics	4
3.2.2 Electron Diffraction Analysis of Cu_{2-x}Se Films	5
3.3 Coulometric Measurements	6
3.4 Band Gap Measurements	7
3.5 Electrical Properties	7
4.0 REFERENCES	8
5.0 PLAN FOR NEXT QUARTER	9

ABSTRACT

The purpose of this program is to investigate the feasibility of using Cu_{2-x}Se as a semiconductor material for the low cost production of photovoltaic solar cells. This report covers the second quarter of the program (August 1, 1979, through November 1, 1979).

The Cu_{2-x}Se films are produced by coevaporation from individually monitored Cu and Se vapor sources. With a substrate temperature of 170°C , single phase cubic Cu_{2-x}Se films have been produced. These films have a direct band gap of 2.2eV and an indirect band gap of 1.4eV.

1.0 SUMMARY

The major results for the reporting period of August 1, 1979, through November 1, 1979, can be summarized as follows:

- A. Cubic phase Cu_{2-x}Se films have been deposited. The films show good uniformity across the substrate.
- B. The deposition conditions necessary to produce cubic phase films have been determined.
- C. The electrical, optical, and physical properties of these films have been measured. The indirect band gap has been determined to be 1.4eV and the direct band gap 2.2eV.

This fulfills the goals that were set for this quarter.

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 by 1980 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 1.29eV^(1,2). Measurements by this laboratory have given values of 1.4eV for the indirect band gap and 2.2eV for the direct band gap. The f.c.c. structure obtained has a lattice constant of $a = 5.76\text{\AA}$. 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.

Specific objectives of this contract are: (1) development of the Cu_{2-x}Se thin film deposition process; (2) characterization of the electrical, optical, and structural properties of the Cu_{2-x}Se films; (3) the fabrication of simple $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ cell structures.

In the previous quarter, progress in the following areas was reported: (1) Vacuum fixturing and setup was completed for the evaporation of Cu and Se from separately controllable sources; (2) A description and theory of the coulometry apparatus was given for the measurement of the composition of the Cu_{2-x}Se films; (3) All films produced were of hexagonal structure.

3.0 TECHNICAL DISCUSSION

3.1 Copper Selenide Film Deposition Procedure

The last Quarterly Report⁽³⁾ discusses the vacuum chamber setup and fixturing for the deposition of Cu and Se from separate vapor sources. The majority of work in this quarter was concentrated on determining the appropriate deposition conditions to produce single phase, cubic structure films.

It has become clear that there is significant reevaporation of material from the film immediately after it is deposited. In the past, up to four separate deposits of different composition were made on each substrate by the use of appropriate masks. Because of the reevaporation problem, only one deposit is now made on a substrate. It appears this change in procedure has been a factor in obtaining cubic phase Cu_{2-x}Se films.

It is apparent that deposition rates for Cu must be on the order of $15\overset{\circ}{\text{A}}/\text{sec}$ at the substrate to avoid producing porous films. A temperature of 170°C at the substrate surface is necessary in order to produce grain sizes of order one micron or greater. The cubic phase structure is produced with rates of the order of $15\overset{\circ}{\text{A}}/\text{sec}$ of Cu and 6 to $8\overset{\circ}{\text{A}}/\text{sec}$ Se. These deposition rates give a stoichiometric parameter x between 0.15 and 0.25. These rates are far from those predicted if one assumed a sticking coefficient of unity for each element. This discrepancy is partly due to the quartz crystals being near room temperature and the substrate at an elevated temperature.

Deposits to date have been made on low cost glass substrates (0211 glass). The low substrate temperature will allow one to deposit the Cu_{2-x}Se onto the CdS if desired. One can then take advantage of the good crystallinity properties of the CdS film.

Since cubic films of Cu_{2-x}Se can be made without close control of the vapor sources, deposition procedures should be simplified. This should be of considerable help in achieving the goal of low cost devices.

3.2 Film Structural Studies

3.2.1 General Characteristics

According to the literature⁽⁴⁾, two stable phases (α , β) of Cu_{2-x}Se exist at room temperature depending on the stoichiometric parameter " x ". The α -phase exists at

room temperature and has a hexagonal lattice with $a = 7.07\text{\AA}$ and $c = 6.68\text{\AA}$ ⁽⁵⁾. The β -phase occurs for $0.20 \leq x \leq 0.25$ and has f.c.c. structure with a lattice constant of 5.7605\AA .

Our cubic phase thin films have an x value of 0.15. Indications are that single phase cubic films may be made in the range of 0.15 to 0.25.

Some of our very thin films ($< 700\text{\AA}$ thickness) show degradation over a 5-day period. It is probable the films are changing from cubic to hexagonal structure⁽⁶⁾. Heat treatment at 100°C in a reducing atmosphere restores the appearance of these films. No extensive work has been done yet on this characteristic. No degradation has been observed to date on films greater than 700\AA in thickness.

3.2.2 Electron Diffraction Analysis of Cu_{2-x}Se Films

The analysis of the deposited copper selenide film crystalline structure by electron diffraction has continued during the second quarter. The standard technique has been to deposit the films onto glass substrates, remove with an HF, water, acetone, glass etchant, and mount on copper grids for transmission electron diffraction (High Resolution) at 100kV. Because extraneous lines were frequently present in the diffraction patterns which appeared to correspond to a hydrated copper silicon fluoride compound, nickel grids have been substituted for the standard copper material.

In order to reduce the deposition cycle time, a series of four films of varied composition (controlled by the copper and selenium deposition rates) was deposited on a single substrate by using metal masks and an 'in situ' mask changer. In some experiments the deposition rates were held constant and the substrate temperature varied to form the four samples. It was determined that temperatures in excess of 160°C were necessary to form well developed polycrystalline structures with grain sizes greater than one micron.

Although the film composition had presumably been varied by the Cu:Se deposition rates, the electron diffraction patterns of all of the initial films were quite similar and showed the predominance of the hexagonal Cu_2Se structure described in the First Quarterly Report. It was subsequently learned that the film composition of the first deposits was altered by being maintained at the elevated substrate temperature for the time necessary to complete the four sample series. By making only a single deposit on each substrate and then cooling the substrate, a correlation was developed between deposition

parameters and film structure. Moreover, the results agreed with the coulometric and optical absorption measurements.

The electron diffraction data on one film deposited at 170°C with Cu and Se deposition rates adjusted such that the coulometric determined 'x' value was 0.15 are presented in Table 1. With this 'x' value, the literature predicts the existence of the cubic Cu_{2-x}Se phase⁽⁴⁾. In Table 1, the 'd' values and relative intensities of the first 16 lines in the electron diffraction pattern are listed. The hkl indices for each line (assuming a face centered cubic structure) are also listed along with the values contained in the ASTM index card for Cu_{2-x}Se (Berzelianite, cubic, $a_0 = 5.739\text{\AA}$, card 6-0680). There is seen to be good agreement with the measured lines and the cubic Cu_{2-x}Se material. No extra lines were present with the exception of lines with 'd' values of 1.66\AA , 1.29\AA , and 0.771\AA . However, these three lines correspond to reflections from the (222), (420), and (642) planes, respectively, for a face centered cubic structure. The high sensitivity of the high resolution electron diffraction technique and/or possible preferred orientation effects may be responsible for the detection of these lines in the present case while not being listed on the ASTM card.

Finally, by using the 'd' and hkl values, the lattice parameter for the deposited cubic material was calculated with the results also displayed in the table. The average value was 5.76\AA which exactly agrees with the parameter for Cu_{2-x}Se material with an 'x' value of 0.15⁽⁶⁾.

3.3 Coulometric Measurements

The coulometry apparatus affords a method by which the stoichiometric index "x" can be measured. A description of the apparatus and theory are detailed in the last Quarterly Report⁽³⁾.

Data taken to date indicates the need for Cu_{2-x}Se films made at deposition rates of order 15Å/sec for Cu. Lower deposit rates lead to porous films. This in turn leads to a "washed out" appearance in the coulometric graphical data.

Actual graphical data for a cubic film with $x = 0.15$ are shown in Figure 1. The values Q_1 and Q_2 are used to determine x from⁽³⁾

$$x = \frac{2Q_1}{Q_1 + Q_2}$$

A graph showing the correlation between the stoichiometric parameter x and the quartz crystals that monitor the deposition is shown in Figure 2. All data for this calibration curve is from deposits that contain 1500\AA of Cu and amounts of Se that vary between 320\AA and 900\AA . We believe that the stoichiometric parameter x in the range 0.15 to 0.25 will give single phase cubic films.

3.4 Band Gap Measurements

The Cary 14 spectrophotometer was used to measure the relative optical transmission as a function of wavelength. With the proper deposition conditions to produce cubic material, a typical curve of absorption versus wavelength is shown in Figure 3a. The films are seen to be quite transparent through the visible spectrum. The absorption at the longer wavelengths is attributed to the free carrier absorption.

The free carrier absorption is given by⁽⁷⁾

$$A \propto \lambda^2$$

where A is the absorbance. A plot of $A^{1/2}$ vs. λ in the long wavelength region is a straight line. This line is then subtracted from the curve in Figure 3a to remove the effect of the free carrier absorption. The results are shown in Figure 3b.

The band gap width can be determined with the aid of the relations

$$A \propto (\hbar\omega - E_g)^{1/2}$$

for the direct band gap and

$$A \propto (\hbar\omega - E_g)^2$$

for the indirect band gap. One then plots A^2 vs. $\hbar\omega$ and $A^{1/2}$ vs. $\hbar\omega$ to determine the energy for the direct and indirect band gap. These results are shown in Figure 4.

The values obtained are:

$$E_{g_{\text{direct}}} = 1.4\text{eV}$$

$$E_{g_{\text{indirect}}} = 2.2\text{eV}$$

These values are obtained for the stoichiometric index in the range $0.17 \leq x \leq 0.25$.

The values for a Cu_2Se film by going through the same process as above yield.

$$E_{g_{\text{direct}}} = 1\text{eV}$$

$$E_{g_{\text{indirect}}} = 2.2\text{eV}$$

3.5 Electrical Properties

The hole mobilities are in the range of $3-7\text{cm}^2/\text{Vsec}$. The hole density is of the order of 4×10^{22} holes/ cm^3 .

4.0 REFERENCES

1. G. P. Sorokin, *IZV. Vyssh. Uchab. Zaved., Fizika*, No. 4, (1965) 140
2. G. P. Sorokin, Hu. M. Papshev, and P. T. Oush, *Sov. Phys. - Solid State (English Translation) I*, (1966), 1810
3. R. A. Mickelsen, W. S. Chen, and J. M. Stewart, "Emerging Systems for Solar Cell Applications - Cu_{2-x}Se ", First Quarterly Technical Progress Report, SERI Contract DE-AC04-79ET23005
4. A. Tonejc, Z. Ogorelec, and B. Mestnik, *Appl. Cryst.* 8, (1975), 375
5. R. B. Shafizade, I. V. Ivanova, and M. M. Kazinets, *Thin Solid Films*, 35, (1976) 169
6. S. G. Ellis, *J. Appl. Phys.* 38 (1967) 2906
7. T. S. Moss, Optical Properties of Semiconductors, Butterworths Scientific, London (1959)

5.0 PLAN FOR NEXT QUARTER

A CdS crystal has been received. Preparations are under way to dice and polish the crystal to make a single crystal cell.

Preparations are under way to include a CdS vapor source within the system. This will then give the capability to produce both CdS/Cu_{2-x}Se thin film devices and single crystal devices. We anticipate making both in the third quarter.

Additionally, more runs with Cu_{2-x}Se will be made to fully explore the possible range of deposition parameters that will give single phase, cubic Cu_{2-x}Se films.

TABLE 1. ELECTRON DIFFRACTION DATA FOR DEPOSITED COPPER SELENIDE FILM

Intensity	'd' Value (Å)	(hkl)	Cubic Cu _{2-x} Se, ASTM		Lattice Parameter (Å)
			d(Å)	I/I ₁	
M	3.33	111	3.33	90	5.77
W	2.87	002	2.88	10	5.74
S+	2.03	022	2.02	100	5.74
M	1.74	113	1.729	80	5.77
W	1.66	(222)	----	---	5.75
W	1.44	004	1.434	30	5.76
M-	1.32	133	1.317	20	5.75
W=	1.29	(420)	----	---	5.77
M	1.18	224	1.171	40	5.78
W	1.109	115	1.105	20	5.76
W+	1.020	044	1.014	10	5.77
W+	0.973	135	0.969	10	5.76
W-	0.910	026	0.908	20	5.76
W-	0.881	335	0.876	10	5.78
W	0.805	117	0.804	10	5.75
M	0.771	(642)	----	---	5.77

5.76⁰Å Ave.

FIGURE 1.

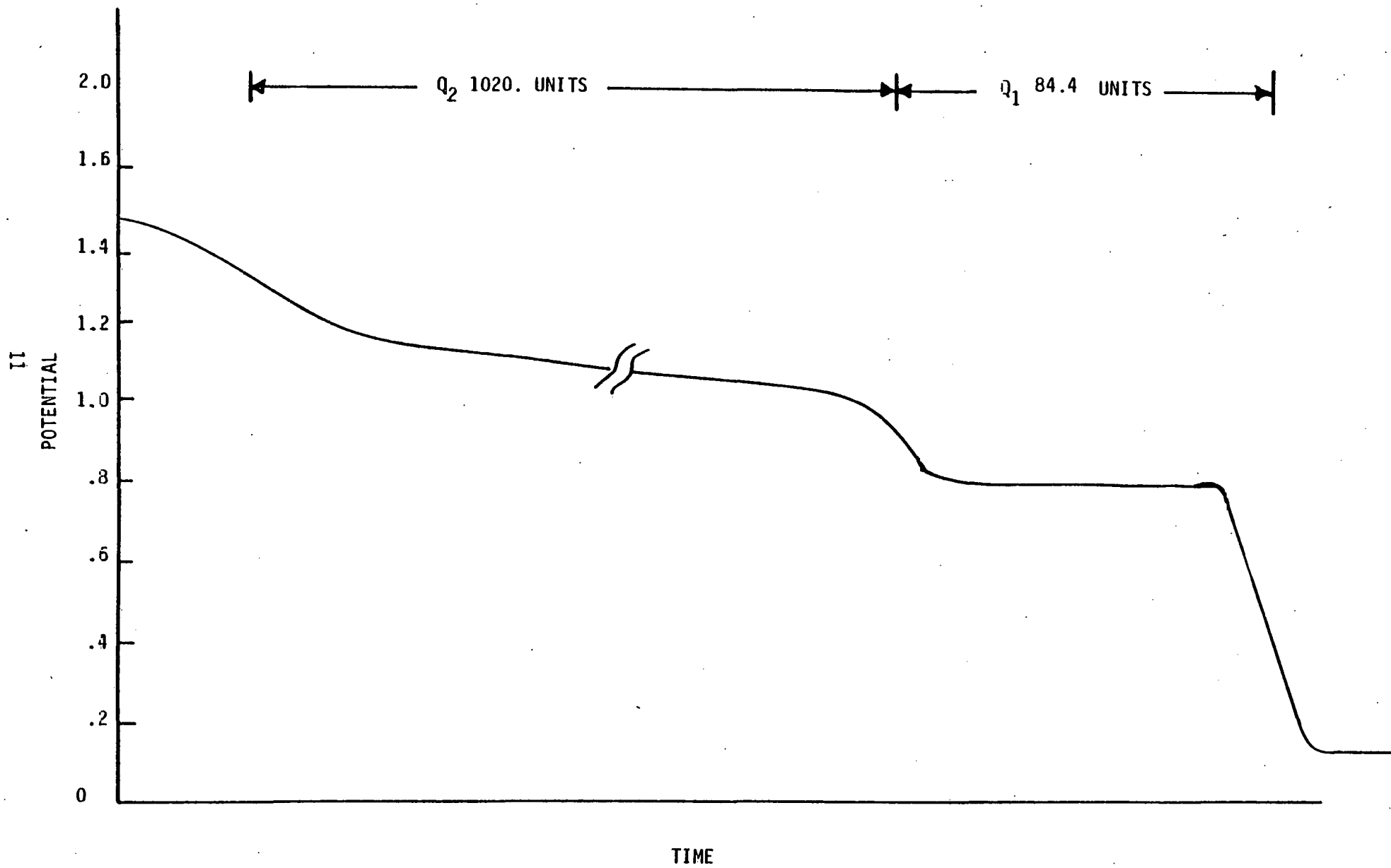


FIGURE 2

Calibration Curve Correlating Quartz Crystal Reading With Stoichiometric Index X.

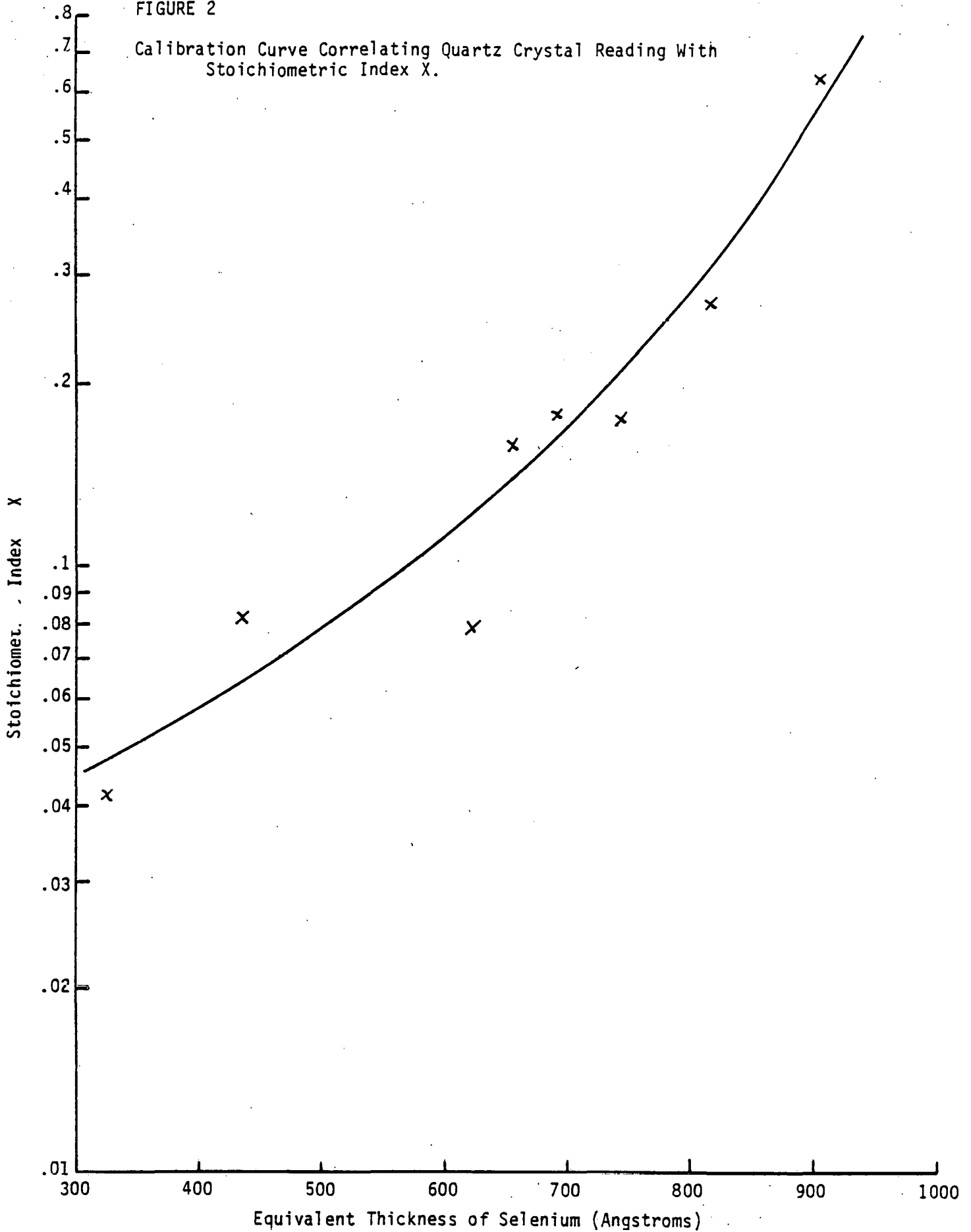


FIGURE 3 Absorbance of $\text{Cu}_{1.83}\text{Se}$ as a Function of Wavelength
(a) As Measured, (b) After Subtracting the Free Carrier Absorption

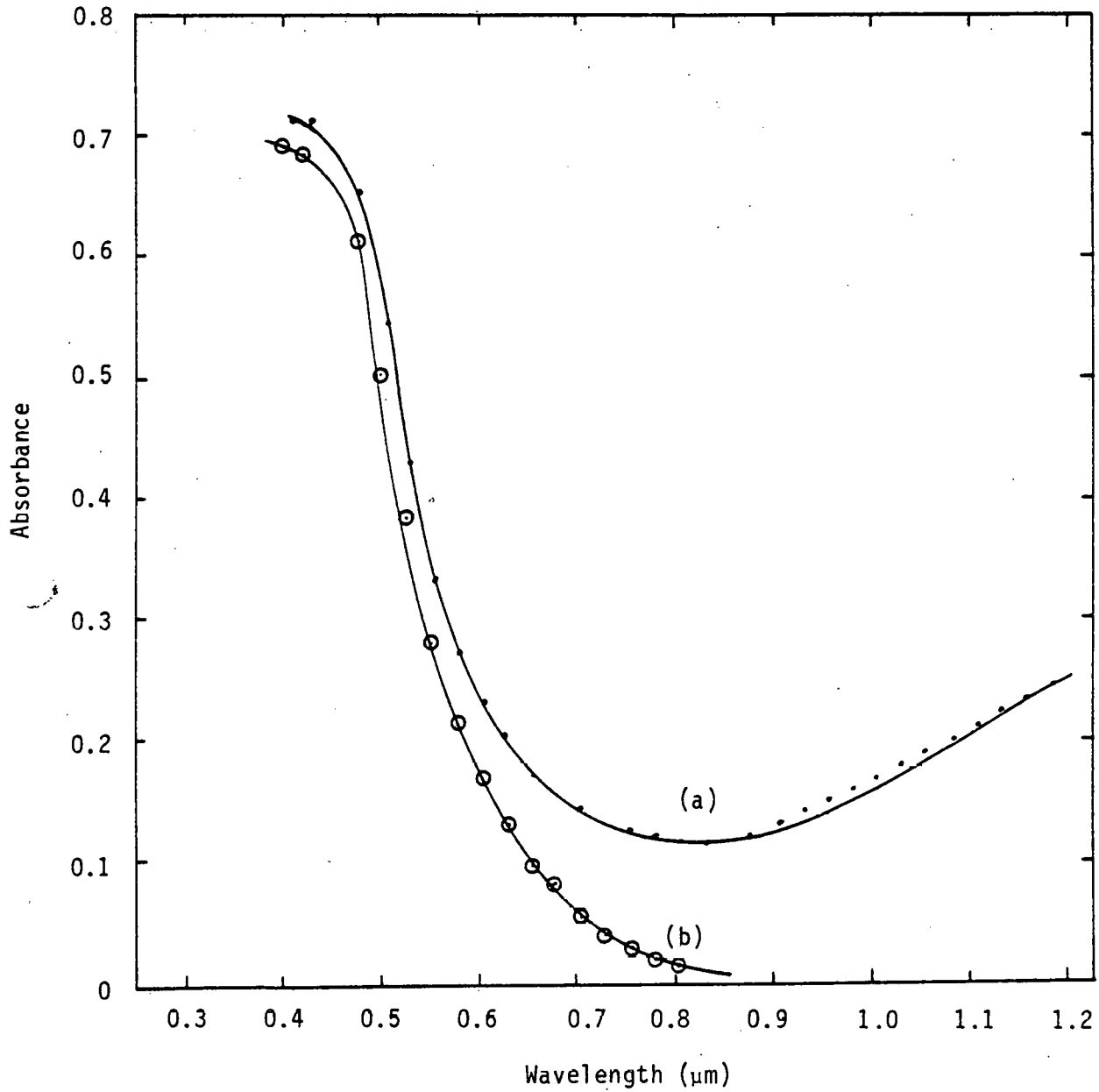


FIGURE 4 Absorbance Data of $\text{Cu}_{1.83}\text{Se}$ Indicating Direct and Indirect Transitions

