SERI/STR-211-3123
DE87001151

February 1987

Deposition of Copper Indium Diselenide Films by Low-Cost Techniques

Final Subcontract Report 15 November 1983 to 14 September 1985

Poly Solar Incorporated
Garland, Texas

Prepared under Subcontract No. XL-4-03125-1

Solar Energy Research Institute
A Division of Midwest Research Institute
1617 Cole Boulevard
Golden, Colorado 80401-3393

Operated for the
U.S. Department of Energy
under Contract No. DE-AC02-83CH10093

NOTICE

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A03

SERI/STR--211-3123

DE87 001151

SUMMARY

Three non-vacuum techniques have been investigated for the deposition of p-$CuInSe_2$ films: (1) the close-spaced chemical vapor transport (CSCVT) technique, (2) the deposition of Cu-In films by the thermal reduction of Cu and In compounds followed by selenization, and (3) the deposition of Cu-In films by electrodeposition followed by selenization.

In the CSCVT technique, polycrystalline plates of $CuInSe_2$ were prepared by direct synthesis from the elements in a fused silica tube and used as the source material of the transport process. Two types of transport apparatus were constructed with similar results. When the source material was of nearly stoichiometric composition, the deposited films were of similar composition, as shown by the electromicroprobe analysis. Using iodine or hydrogen iodide as the transport agent, the nearly optimum conditions for the deposition of p-$CuInSe_2$ films on alumina, graphite, W/Al_2O_3, and Mo/glass substrates were developed. The x-ray diffraction spectra of all films are in agreement with the reported data. The $CuInSe_2$ films deposited from nearly stoichiometric p-$CuInSe_2$ source material were of p-type conductivity. The average electrical resistivity of p-$CuInSe_2$ films on alumina and graphite substrates have been measured. Heterojunction solar cells from cast $CuInSe_2$ ingots and CSCVT $CuInSe_2$ films were made by using CdS as the heterojunction partner. While the open-circuit voltage of solar cells from cast $CuInSe_2$ ingot was usually 420-450 mV under simulated AM1 conditions, the characteristics of solar cells from $CuInSe_2$ films were poor. The conversion efficiency of the best solar cell of 1 cm^2 area was about 2.5%. The inclusion of iodine or other impurities in the transported films could be responsible for the observed results.

The thermochemistry of Cu and In compounds suggests the use of the thermal reduction of a mixture of $Cu(NO_3)_2$ and $In(NO_3)_2$ for the deposition of Cu-In alloys on conducting or insulating substrates. The important process parameters of this process have been investigated, and microchemical analytical techniques were used to determine the composition of Cu-In alloy films deposited on substrates. The selenization of Cu-In films was carried out in a H_2 + H_2Se atmosphere at 400°-500°C. A pronounced loss of indium selenide was observed at 400°C or higher, and an In-rich alloy film must be used for the deposition of nearly stoichiometric $CuInSe_2$ films. The photoresponse of solar cells prepared from these films were poor due presumably to composition inhomogeniety and uncontrolled resistivity.

Electroplating was also used for the deposition of Cu-In films from acid solutions of copper sulfate and indium sulfamate, respectively. The uniformity of the plated films is determined by the geometry of the system, including the shape and size of their electrodes and their conductivity. The Cu/In molar ratio can be controlled within ±2%. The selenization of electroplated Cu-In alloy films is similar to that of chemically reduced Cu-In alloy films in that the vaporization of indium selenide becomes appreciable at selenization temperatures of 400°C or higher. Using cadmium sulfide as a heterojunction partner, the best solar cell of 1 cm^2 area has an AM1 efficiency of about 3%. Further improvement of processing techniques is believed to be capable of increasing the conversion efficiency significantly.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SECTION 1.0

INTRODUCTION

This is the Final Technical Report of a research program on copper indium diselenide ($CuInSe_2$) films supported by the Solar Energy Research Institute under Subcontract No. XL-4-03125-1. The objectives of this program are to prepare device quality thin film polycrystalline $CuInSe_2$ by low-cost techniques and to produce heterojunction solar cells of 1 cm^2 area with an AM1 efficiency of 8% or higher.

Copper indium diselenide, a direct gap semiconductor with a room temperature bandgap of about 1 eV, has been demonstrated to be a most promising thin film photovoltaic material. Considerable amounts of research and development on the fabrication and characterization of thin films $CuInSe_2$ solar cells have been carried out during the past few years. Heterojunction solar cells of the configuration n-CdS/p-$CuInSe_2$ and n-$Cd_xZn_{1-x}S$/p-$CuInSe_2$, deposited by the vacuum evaporation technique, have exhibited AM1 efficiencies of near 12%. Thus far, the vacuum technique has been the major technique for the fabrication of high efficiency cells. Because of the great potential of $CuInSe_2$ films for terrestrial applications, alternatives to the vacuum techniques should be investigated.

In this work, three approaches were used for the deposition of p-type $CuInSe_2$ films: close-spaced chemical vapor transport (CSCVT), thermal reduction of Cu and In compounds followed by selenization, and electroplating of Cu and In films followed by selenization. To produce efficient solar cells, the electrical and structural properties of $CuInSe_2$ films must be controlled. During the course of this program, the important process parameters for (1) the deposition of $CuInSe_2$ films by the CSCVT technique, (2) the deposition of Cu-In films by chemical reduction and electroplating, and (3) the formation of $CuInSe_2$ films by the selenization of Cu-In films have been investigated. Many p-$CuInSe_2$ films have been deposited on conducting and insulating substrates, and their properties have been characterized. Heterojunction solar cells have been fabricated from p-$CuInSe_2$ films prepared by the three techniques, and their photovoltaic characteristics evaluated. The procedures and results are summarized in the following sections.

SECTION 2.0

$CuInSe_2$ FILMS BY CLOSE-SPACED CHEMICAL VAPOR TRANSPORT

The close-spaced chemical vapor transport (CSCVT) technique developed during the early sixties for the epitaxial growth of III-V compounds(1) has been applied to the deposition of thin films of many electronic materials. In this technique, the source and substrate are separated by only a fraction of a millimeter, and all components of the source material are directly transported to the substrate surface independent of the conditions elsewhere in the system. The source material is utilized efficiently, and the deposition process is essentially diffusion-limited.

2.1 SOURCE MATERIAL FOR CSCVT

The source material for the deposition of $CuInSe_2$ films by the CSCVT technique was prepared by the direct combination of the elements in a carbon-coated fused silica tube of rectangular cross-section, 2.5 cm x 1.5 cm. Weighed quantities of copper, indium, and selenium, all of $99.999^{+}\%$ purity purchased from ASARCO Incorporated, were placed in the fused silica tube, evacuated to a pressure of 10^{-6} Torr or less, and sealed while under evacuation. The reaction tube was heated in a resistance-heated furnace at 1050°C to yield $CuInSe_2$ ingots, usually 15 cm long, 2.5 cm wide, and 3-5 mm thick.

To determine the effects of the composition of the source material on the properties of transported films, a number of copper, indium, and selenium mixtures of various molar ratios were used in the synthesis of $CuInSe_2$ ingots. When the composition of the reaction mixture differs appreciably from the stoichiometric ratio, additional phases were detected by electron microprobe analysis carried out at SERI although x-ray diffraction cannot detect these phases due to their low concentrations. The microprobe analysis was carried out using a 25 keV 50 nA electron beam of about 1 mm diameter, and the detection limits for copper, indium, and selenium are 0.02, 0.03, and 0.12 wt%, respectively. Table 2-1 shows the compositional analysis of several $CuInSe_2$ ingots. When the reaction mixture was copper-deficient (source materials 1, 2, and 3), the resulting ingots contained, in addition to $CuInSe_2$, indium selenides (indium forms at least four selenides: In_2Se, $InSe$, In_5Se_6, and In_2Se_3). With the exception of sources 1 and 2, the composition of the ingot determined by the microprobe analysis is in good agreement with that of the reaction mixture used in the synthesis of the ingot. Single-phase large grain (several millimeters and larger) polycrystalline $CuInSe_2$ ingots were obtained over a limited range of reactant composition.

The source material used for most transport experiments was prepared by using a Cu/In molar ratio of unity in the reaction mixture. The conductivity type and electrical resistivity of the $CuInSe_2$ ingot are then determined by the selenium content in the reaction mixture. Selenium deficiency in the reaction mixture yields n-type $CuInSe_2$ while selenium excess yields p-type material. The resistivity of the p-type material, as measured by the four-point probe technique, decreased with increasing selenium concentration.

The room temperature Hall mobility of the p-type ingots is in the range of 5-8 cm^2/V-sec.

Table 2-1. Composition of $CuInSe_2$ Ingots as a Function of Reactant Composition by Electron Microprobe Analysis (Atomic Percent)

	Composition of Reactant				Composition of Ingot		
	Cu	In	Se		Cu	In	Se
Source Material No. 1	19	32	49	phase 1	24.1±0.19	25.76±0.20	50.14±0.40
				phase 2	0.11	56.65±0.99	43.24±0.75
Source Material No. 2	21	30	49	phase 1	24.43±0.34	25.69±0.36	49.88±0.70
				phase 2	0.39±0.01	56.54±1.13	43.08±0.86
Source Material No. 3	23	27.5	49.5	phase 1	23.06±0.17	26.31±0.19	50.63±0.36
				phase 2	1.08±0.20	56.18±1.63	42.74±0.1.18
Source Material No. 4	24	26.5	49.5		23.52±0.20	25.92±0.23	50.57±0.44
Source Material No. 5	25	25	50		25.48±0.07	24.66±0.07	49.86±0.14

2.2 DEPOSITION OF $CuInSe_2$ FILMS BY CSCVT

Iodine has been demonstrated as an effective transport agent for the crystal growth of $CuInSe_2$ platelets.(2) In this work, hydrogen iodide was also used as the transport agent because of the ease of controlling its partial pressure. The reaction between $CuInSe_2$ and HI is very similar to that between $CuInSe_2$ and I_2 since hydrogen iodide dissociates partially into its elements at high temperatures. The use of other transport agents was explored without success. For example, no transport of $CuInSe_2$ was observed when hydrogen chloride or hydrogen bromide was used as the transport agent due to the chemical inertness of $CuInSe_2$ toward HC and HBr.

Because of the chemical reactivity of iodine and hydrogen iodide at the temperatures used in the transport process, 500°-600°C, the selection of the substrate is limited. For example, refractory metals such as molybdenum and tungsten are converted into volatile iodides. Alumina and graphite were used as substrates in most deposition experiments. Since the surface of graphite substrates has a high concentration of pits due to its porosity and the pits may interfere with the nucleation of $CuInSe_2$, the substrate surface was coated with a thin layer (1-2 μm) of carbon by the pyrolysis of propane at 1100°C or a thin layer of silicon carbide by the pyrolysis of dimethyldichlorosilane. The coated graphite provides a more homogeneous surface for the nucleation and growth of $CuInSe_2$ films. The CSCVT process was carried out in a vertical or horizontal fused silica reaction tube, as shown in Figures 2-1 and 2-2, respectively.

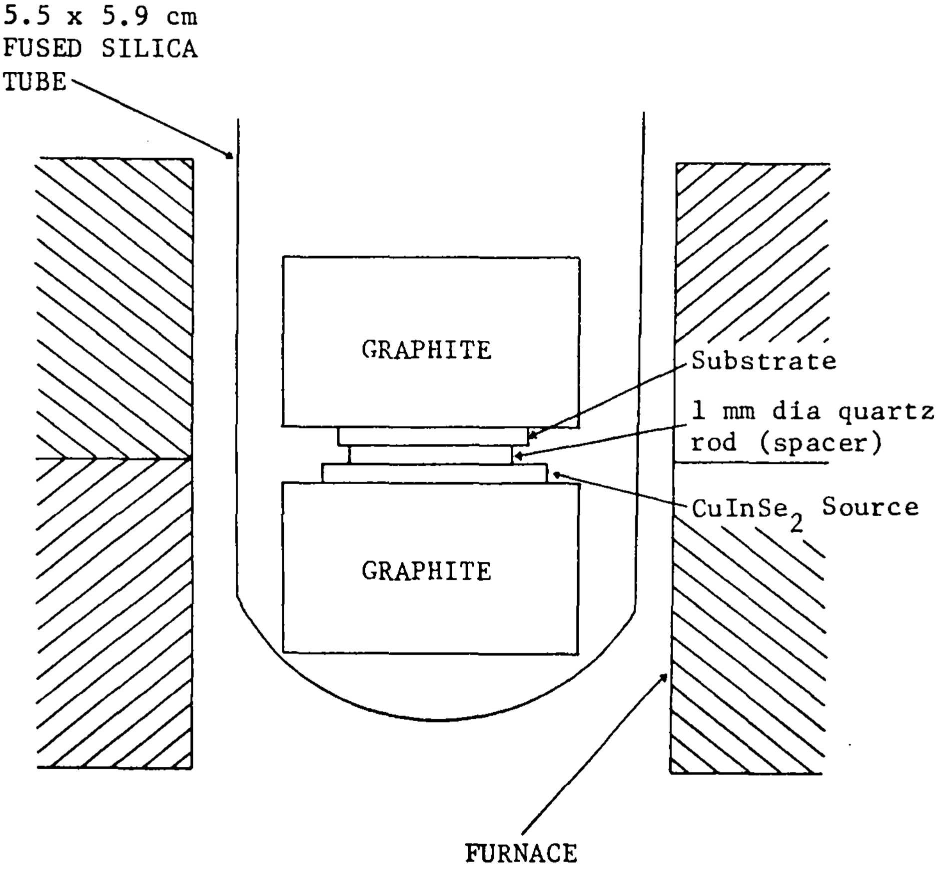

Figure 2-1. Schematic Diagram of the Vertical Apparatus for the Deposition of $CuInSe_2$ Films by CSCVT

Two separately heated and independently controlled heaters were used to maintain the source material and the substrate at the desired temperature. The heater material is an important consideration; it should be impervious and chemically inert. Single-crystalline silicon was first used as heaters; however, silicon readily forms silicon selenide which hydrolyzes in the laboratory ambient, liberating hydrogen selenide. Silicon dioxide and sili-

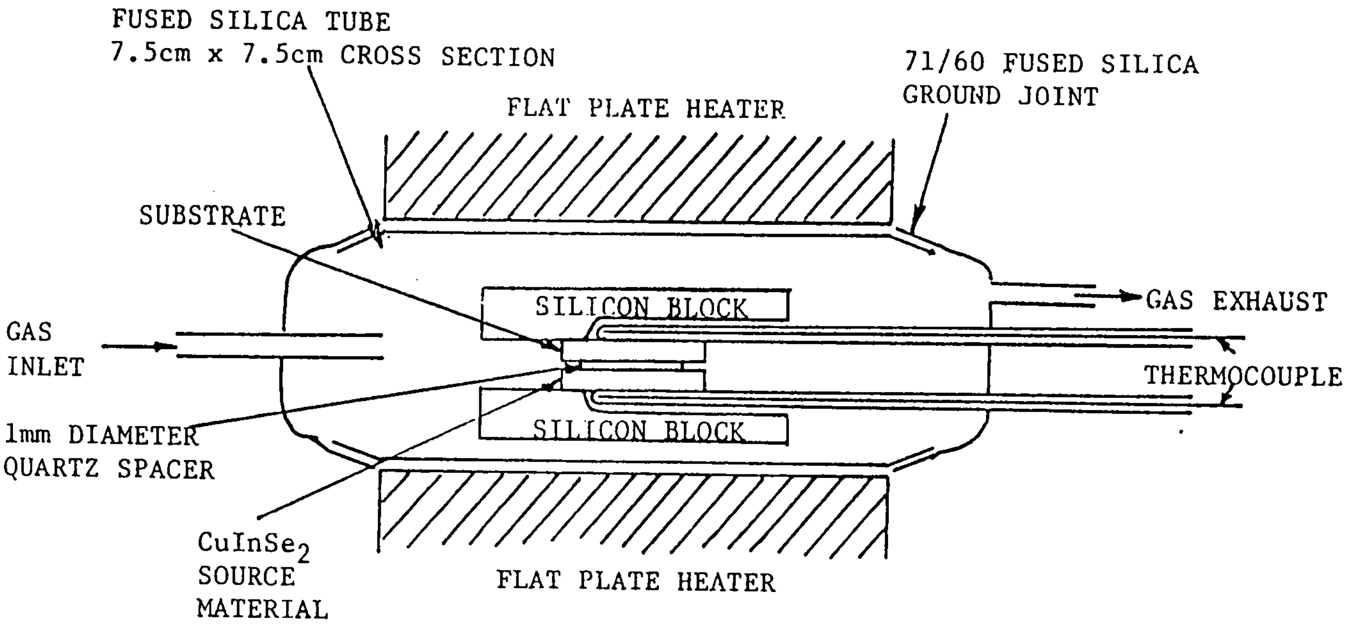

Figure 2-2. Schematic Diagram of the Horizontal Apparatus for the Deposition of $CuInSe_2$ Films

con nitride-coated silicon blocks were also found to be unsuitable because of pinholes in the coating. Graphite is porous, and the coating of high density graphite with about 150 μm of silicon carbide is better-suited as the heaters. Quartz rods of 0.1 cm diameter were used as spacers between the source material and the substrate. The entire assembly was enclosed in a fused silica tube provided with gas inlet and outlet tubes. Thermocouples were used to monitor the temperatures of the substrate and the source material.

The important parameters in the CSCVT technique are the substrate temperature, the temperature difference between the source and the substrate, the separation between the source and the substrate (fixed at 0.1 cm for convenience), and the partial pressure of the transport agent. Many CVCVT experiments were carried out to determine the range of process parameters required for the deposition of uniform $CuInSe_2$ films. The use of the vertical or horizontal reaction tube and the use of I_2 or HI as the transport agent have produced essentially the same results. The source temperature and the pressure of the transport agent are important in that they determine the reaction rate between the source material and the transport agent. Source temperature in the range of 500°-600°C and I_2 or HI partial pressure of 200-300 Torr were found to be suitable. At low source temperatures, 450°C for example, the rate is too slow for depositing continuous films. At too high temperatures, such as 650°C, the selenium dissociation pressure becomes appreciable and the deposited films were selenium deficient. The substrate temperature determines the rate of nucleation and the grain size in $CuInSe_2$ films. The use of low substrate temperatures favors the nucleation process and the formation of small grains in the films. The nucleation rate is reduced and the grain size is increased at high substrate temperatures; however, the film may not become continuous until a large thickness is deposited. The temperature difference between the source and the substrate also determines the deposition rate of $CuInSe_2$ films, and a 20°-30°C temperature difference was used in most experiments.

2.3 Properties of Transported $CuInSe_2$ Films

Adherent and uniform $CuInSe_2$ films have been deposited on alumina, graphite, and SiC/graphite substrates over the temperature range of 500°-600°C using a H_2-HI mixture containing about 30% HI (pinholes frequently observed at HI concentrations below 30%). $CuInSe_2$ films are not adherent to C/graphite due presumably to the difference in thermal expansion coefficients. No quantitative correlations between the deposition rate and the process parameters were made because of the difficulties in reproducing the temperature gradient over a wide temperature range. Using a H_2-30% HI mixture as the transport agent, for example, the deposition rates of $CuInSe_2$ films on alumina substrates were approximately 13, 20, and 23 μm/hr at 520°, 550°, and 570°C, respectively. The deposition rate was found to decrease at temperatures higher than 600°C.

The microstructure of $CuInSe_2$ films depends strongly on the substrate temperature, as expected. Using a H_2-HI mixture containing 30% HI, the average grain size in $CuInSe_2$ films deposited on graphite substrates at 500°C is 3-4 μm and increases to 15-20 μm in films deposited at 600°C. Further, under the same deposition conditions, the nucleation and growth of $CuInSe_2$ are also affected or SiC/graphite substrates exhibit more densely packed structure than those on graphite substrates. Figure 2-3 shows the scanning electron micrographs of $CuInSe_2$ films deposited on graphite and alumina substrates. The $CuInSe_2$ films deposited on alumina substrates at high temperatures also shows a columnar structure (Figure 2-4).

The composition of a number of $CuInSe_2$ films deposited on graphite and alumina substrates under a wide range of conditions was determined by the electron microprobe technique. Nearly stoichiometric films were obtained in all cases as long as the source material did not deviate appreciably from the stoichiometric composition. This is demonstrated in Table 2-2, where $CuInSe_2$ films of very similar compositions were deposited on graphite substrates at 570°C from three source materials of different composition. Iodine on the order of 0.2 atomic percent was also detected in $CuInSe_2$ films from microprobe and SIMS measurements.

The crystallographic properties of $CuInSe_2$ films deposited on graphite and alumina substrates have been determined by the x-ray diffraction technique using CuKα radiation. The diffraction spectra of all films examined are similar, except in relative intensities. Table 2-3 summarizes the data obtained from a $CuInSe_2$ film on a graphite substrate. The "d" values are in agreement with the published data.(3)

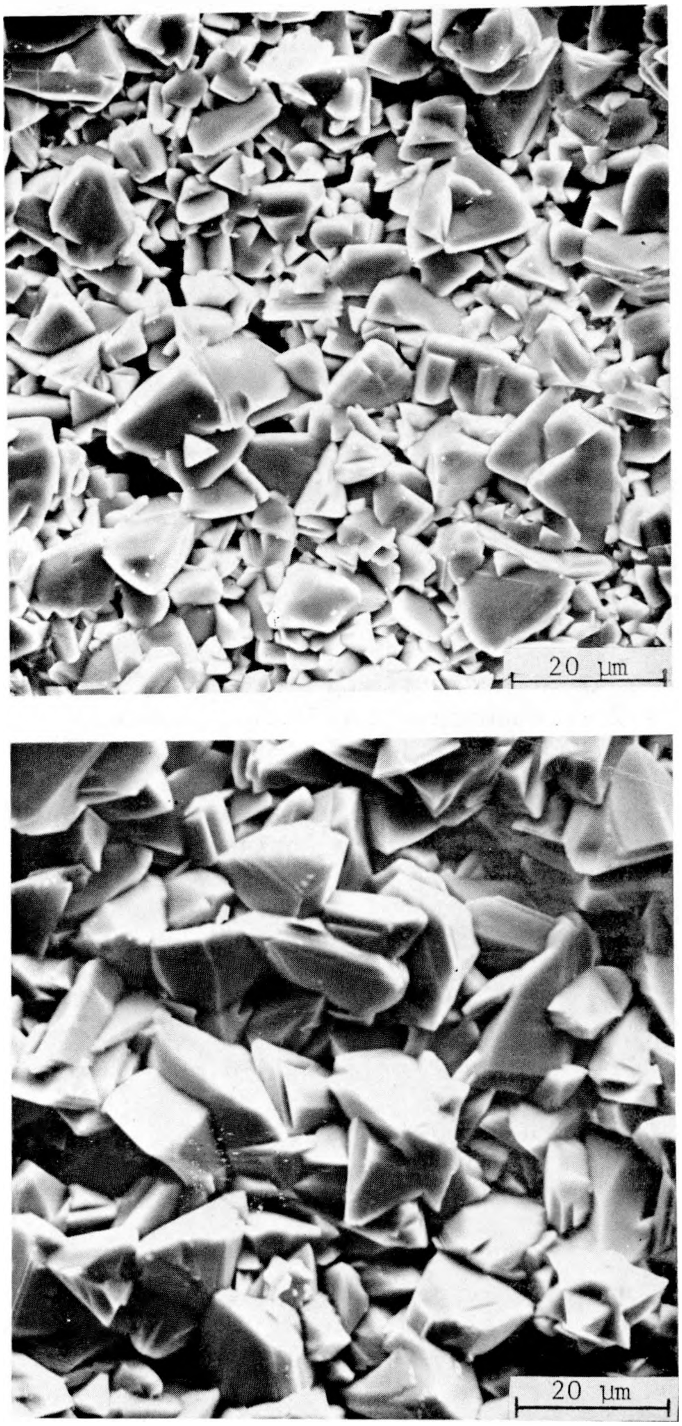

Figure 2-3. Scanning electron micrographs of $CuInSe_2$ films deposited on graphite (upper) and alumina (lower) substrates

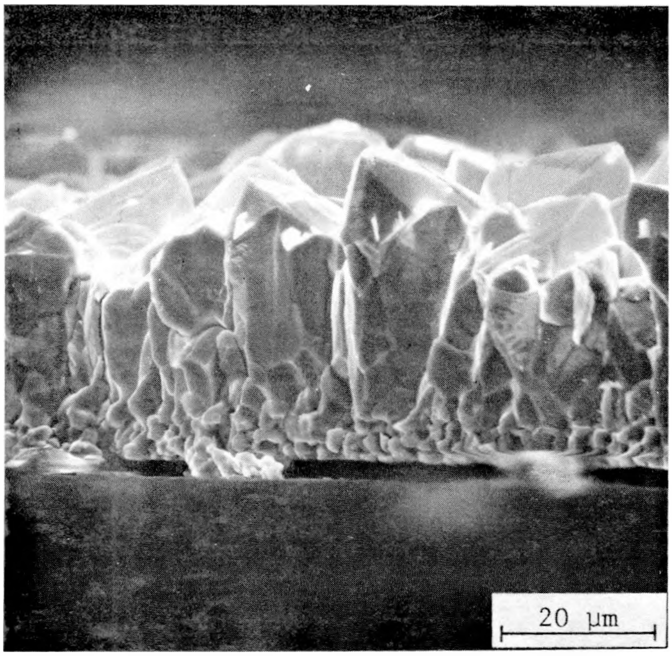

Figure 2-4. **Vertical cross section of a $CuInSe_2$ film on an alumina substrate showing the columnar growth of $CuInSe_2$**

Table 2-2 Composition of $CuInSe_2$ Ingots and Transported Films By Electron Microprobe Analysis (Atomic Percent)

Composition of Source Material			Composition of Transported Film		
Cu	In	Se	Cu	In	Se
23.13±0.25	26.23±0.28	50.64±0.54	25.18±0.82	25.44±0.83	49.38±1.61
23.88±0.35	25.97±0.38	50.15±0.74	25.39±0.80	25.35±0.80	49.26±1.56
25.48±0.17	24.66±0.17	49.86±0.24	25.09±0.38	24.94±0.38	49.98±0.76

Using nearly stoichiometric p-type $CuInSe_2$ ingots of 5-20 ohm-cm resistivity as the source material, all transported films are of p-type conductivity. The electrical resistivity of $CuInSe_2$ films on alumina substrates was measured by the four point probe technique, and the lateral resistivity profile was readily obtained. To determine the resistivity of $CuInSe_2$ films on graphite substrates, silver contacts of about 0.5 cm diameter were evaporated onto the surface of the films and heated in helium at 300°C. By passing current through the thickness direction of Ag/$CuInSe_2$/graphite structures, the potential drops between Ag and $CuInSe_2$ and between Ag and graphite were measured to yield the Ag/$CuInSe_2$ interface resistance and the sum of $CuInSe_2$ resistance and the $CuInSe_2$/graphite interface resistance. The resistivity of $CuInSe_2$ was deduced by assuming negligible $CuInSe_2$/graphite interface resistance.

Table 2-3. Powder Diffraction Data of $CuInSe_2$ and a $CuInSe_2$ Film on Graphite Substrate

Standard Data			Observed	
d	hkl	I/I_o	d	I/I_o
5.20	101	5	5.124	8
3.34	112	70	3.321	100
3.20	103	5	3.194	12
2.52	211	15	2.516	2
2.15	105 213	5	2.138	3
2.04	204 220	100	2.039	90
1.90	301	5		
1.743	116 312	85	1.741	40
1.480	323 305	5		
1.446	400 008	25		
1.327	332 316	35	1.325	35
1.1813	424	60	1.180	20
1.1137	512 336	25	1.114	15
1.0245	048	20	1.022	10

The average electrical resistivities of $CuInSe_2$ films on graphite and alumina substrates as a function of deposition temperature are shown in Figures 2-5 and 2-6, respectively. The resistivity of $CuInSe_2$ films on alumina substrates is many times higher than that of the source material, and resistivity inhomogeneities are frequently observed in various regions of a specimen, particularly in high resistivity materials. The high resistivity of $CuInSe_2$ films on alumina substrate could be related to the grain boundaries since the four probe measurements include the contribution of potential barriers at the boundaries. The high resistivity could also be related to selenium deficiency in $CuInSe_2$ films, as suggested by the increase of resistivity with increasing temperature. The resistivity of $CuInSe_2$ films on alumina substrates may be reduced by heating the film in a hydrogen-selenium mixture containing about 0.03% selenium at 750°C, as shown in Figure 2-7. At lower temperatures, 600°C for example, the resistivity of $CuInSe_2$ films was not affected by selenium treatment. Under the same deposition

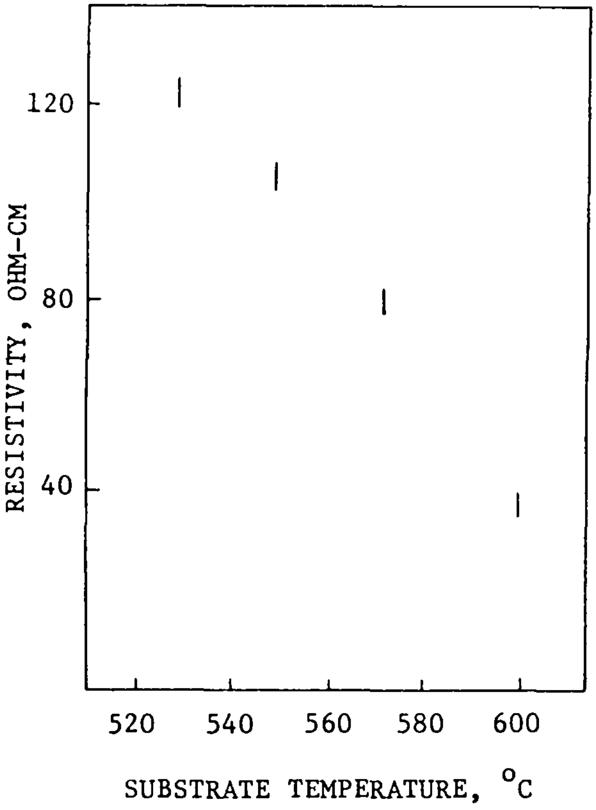

Figure 2-5. Electrical resistivity of $CuInSe_2$ films on graphite substrates as a function of deposition temperature.

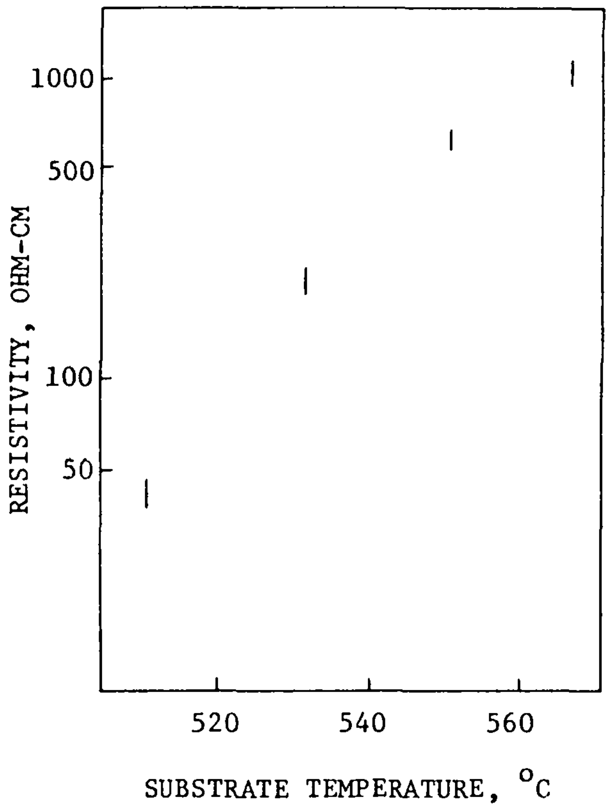

Figure 2-6. Electrical resistivity of $CuInSe_2$ films on alumina substrates as a function of deposition temperature.

conditions, the resistivity of $CuInSe_2$ films on graphite substrates is appreciably lower than that on alumina substrates due partly to the fact that the measurements in the thickness direction of the film exclude the effects of potential barriers at grain boundaries. Further, carbon may act as an acceptor in $CuInSe_2$, as suggested by the decreasing resistivity with increasing temperature (carbon has been shown to be electrically active in cadmium telluride films.)

2.4 PHOTOVOLTAIC CHARACTERISTICS OF $CuInSe_2$ FILMS

The photovoltaic characteristics of $CuInSe_2$ ingot and transported films have been investigated. Heterojunction solar cells were prepared by depositing a thin film of cadmium sulfide without intentional doping (resistivity: 2-5 ohm-cm) onto the surface of $CuInSe_2$ using vacuum evaporation. Thin films of zinc oxide deposited by ion-beam sputtering (resistivity: 0.01-.03 ohm-cm) were also used as the heterojunction partner in some cases. The solar cells prepared from cast $CuInSe_2$ ingots showed open-circuit voltages of 420-450 mV under simulated AM1 conditions using quartz-halogen lamps. The photocurrent and fill factors of these cells were not measured because of the high resistivity of $CuInSe_2$ ingots.

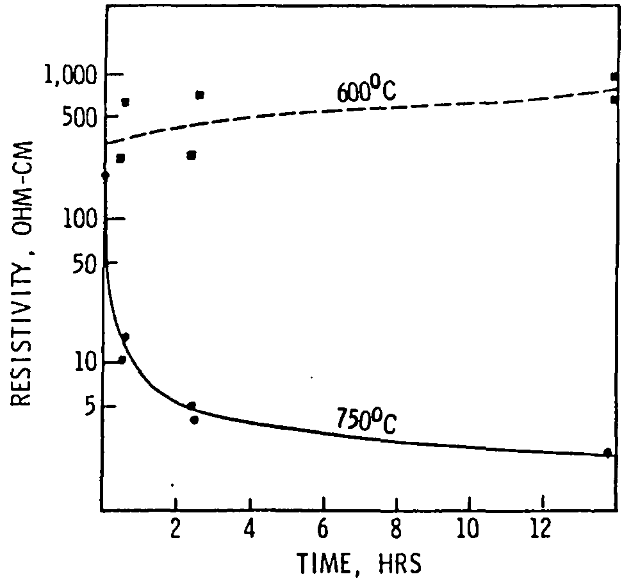

Figure 2-7. Effect of selenium treatment at high temperatures on the resistivity of $CuInSe_2$ films on alumina substrates

Because of the reactivity of most metals toward hydrogen iodide at high temperatures, it was not possible to deposit a metal interlayer between $CuInSe_2$ and alumina substrates, as used by other investigators.(4) Thin film heterojunction solar cells were therefore prepared from $CuInSe_2$ films deposited on graphite substrates; the resistivity of $CuInSe_2$ films was controlled by controlling the substrate temperature. About twenty solar cells were prepared; the open-circuit voltages, short-circuit current densities, and fill factors under simulated AM1 conditions were in the ranges of 150-250 mV, 10-26 mA/cm^2, and 35-45%, respectively. The best cell of 1 cm^2 area has a conversion efficiency of about 2.5%, which is considerably lower than that reported for heterojunction cells prepared by vacuum evaporation. Since the open circuit voltage of solar cells prepared from CSCVT $CuInSe_2$ films is considerably lower than that from melt-grown $CuInSe_2$ ingots, it is possible that iodine included in the transported films may reduce the minority carrier diffusion length in $CuInSe_2$. The use of graphite substrates may also introduce lifetime-killing impurities.

In spite of the usefulness of the CSCVT technique for the deposition of nealy stoichiometric $CuInSe_2$ films at relatively high rates, the heterojunction solar cells prepared from $CuInSe_2$ films deposited under a reasonable range of process parameters do not have conversion efficiencies comparable to those prepared by vacuum evaporation. Investigations of the process parameters responsible for the poor photoresponse of CSCVT $CuInSe_2$ films could be very time-consuming. It may be more productive to focus further efforts to the development of other low-cost techniques for the deposition of $CuInSe_2$ films.

SECTION 3.0

$CuInSe_2$ FILMS BY SELENIZATION OF CHEMICALLY REDUCED Cu-In FILMS

In view of the poor photovoltaic characteristics of $CuInSe_2$ films deposited by the CSCVT technique, alternate low-cost approaches for the deposition of $CuInSe_2$ films have been explored. Considerable efforts were directed to determine the most economical and reproducible techniques for the deposition of device-quality $CuInSe_2$ films on metal-coated ceramic or glass substrates. The deposition of Cu-In alloy films on the substrate followed by the selenization of the resulting film appears to be most attractive. The Cu-In phase diagram (Figure 3-1)(5) suggests that the Cu-In film must be heated above

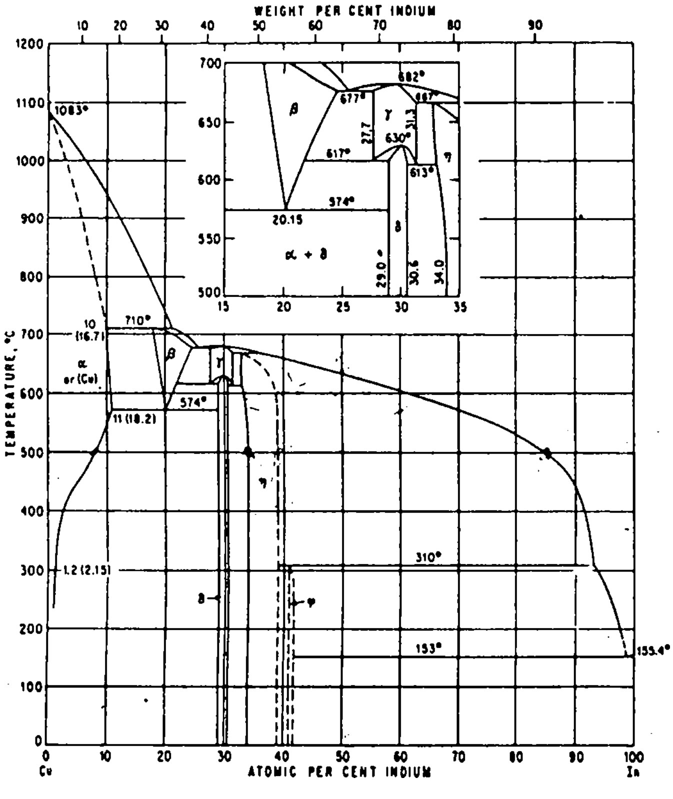

Figure 3-1. The Cu-In phase diagram

the melting point of equi-molar Cu-In alloy, about 630°C, in order to obtain a single-phase material. Cu-In alloy films may be deposited by several methods; the chemical method, using the thermal decomposition or reduction of Cu and In compounds, is most economical and readily scalable. The deposition of Cu-In films by the chemical method, the selenization of Cu-In films, and the properties of the resulting films are discussed in this section.

3.1 DEPOSITION OF CU-IN FILMS BY CHEMICAL METHOD

In general, chemical processing is of lower cost than vacuum techniques. Many copper and indium compounds of relatively high purity (99.99$^+$%) are available at reasonable costs and may be used for the preparation of thin films of Cu-In alloys on suitable substrates. It is essential that the copper and indium compounds have negligible vapor pressure at temperatures used for the reduction or decomposition process (400°-500°C for example), and that the reduction or decomposition process involves no undesirable side-products. When these criteria are met, the utilization of the Cu and In compounds is essentially 100%, providing a truly low-cost process. However, the thermochemical data of copper and indium compounds are incomplete, and little information is available on high temperature solid state reactions involving these compounds. The potentially useful Cu and In compounds and their room temperature thermochemical properties are summarized in Table 3.1 and 3.2, respectively.(6) While most of the Cu compounds, such as the halides, are readily reduced to the metal by heating in a hydrogen atmosphere because of the favorable free energy changes, the halides are not suitable for the preparation of Cu-In alloys since they have relatively low melting point and may partially vaporize before the reduction is complete. Copper sulfate is relatively stable as indicated by its large free energy of formation. The remaining compounds, such as Cu_2O and CuO, are readily reduced at temperatures below 300°C, and $Cu(NO_3)_2$ decomposes into the oxide at temperatures below 300°C. $Cu(NO_3)_2$ is soluble in water and alcohol while Cu_2O is soluble in aqueous ammonia solution. The selection of the indium compounds is encountered with similar problems; the halides are volatile and may vaporize before reduced in hydrogen. The sulfate has a very large free energy of formation. The oxide has negligible vapor pressures at temperatures below 600°C and may be reduced by hydrogen at about 500°C; however, it is insoluble in water or organic solvents. The nitrate decomposes into oxide at 300°-400°C and is soluble in water and alcohol. Thus, the oxides and nitrates are better suited for the preparation of Cu-In alloys than others. When the Cu compound is reduced to the metal, its vapor pressure is negligible. However, the vapor pressure of In is considerably higher than that of Cu, and precautions must be taken to minimize the vaporization of indium. The vapor pressures of Cu and In in the temperature range of 400°-700°C are shown in Figure 3-2.

The amount of Cu and In compounds required for the deposition of Cu-In alloys on substrates is very small. For example, 1.4×10^{-5} moles of copper compound is required to produce 1 μm of Cu per square centimeter of the substrate, assuming that the Cu compound is quantitatively reduced. The amount of In compound required to produce 1 μm of In per square centimeter of the substrate is only 6.36×10^{-6} moles. Ceramic substrates of 6 cm^2 area coated with 1-2 μm of tungsten have been used for the deposition of Cu-In alloy films. Thus, 4.2×10^{-5} moles of each are required to produce 0.5 μm of Cu and 1.1 μm of In per substrate, forming stoichiometric Cu-In alloy. If one wishes to use 0.1 ml of each solution, the concentration of the Cu compound and In compound is 0.42 M. Since the commercial Cu and In compounds usually contain varied amount of water crystallization, the concentration of Cu^{+2} and In^{+3} in solutions must be accurately determined. The

Compound	M.P., °C	H_f^o kJ/mole	G_f^o kJ/mole	S^o J/mole°K	Cp J/mole°K
CuO	1326	-157.3	-129.7	42.63	42.30
Cu_2O	1235	-168.6	-146.0	93.14	63.64
$CuCl$	430	-137.2	-119.86	86.2	48.5
$CuCl_2$	620	-220.1	-175.7	108.07	71.88
$CuBr$	492	-104.6	-100.8	96.11	74.73
$CuBr_2$	498	-141.8			
CuI	605	-67.8	-69.5	96.7	54.06
CuS		-53.1	-53.6	66.5	47.82
Cu_2S	1100	-79.5	-86.2	120.9	76.32
$CuSO_4$		-771.36	-661.8	109	100
$CuSe$		-39.54			
Cu_2Se	1113	-39.54			
$Cu(NO_3)_2$		-302.9			

Table 3-1. Thermochemical Data of Crystalline Copper Compounds at 298°K

Compound	M.P., °C	H_f^o kJ/mole	G_f^o kJ/mole	S^o J/mole°K	Cp J/mole°K
In_2O_3	volatile at 850	-925.79	-830.68	104.2	92
$InCl$	225	-186.2			
$InCl_3$	586	-537.2			
$InBr$	220	-175.3	-169.0	113	
$InBr_3$	436	-428.9			
InI	351	-116.3	-120.5	130	
InI_3	210	-238			
InS	692	-138.1	-131.8	67	
In_2S_3	1050	-427	-412.5	163.6	117.99
$In_2(SO_4)_3$		-2787	-2439	272	280
$InSe$		-117			
In_2Se_3	890	-343			
$In(NO_3)_3$					

Table 3-2. Thermochemical Data of Crystalline Indium Compounds at 298°K

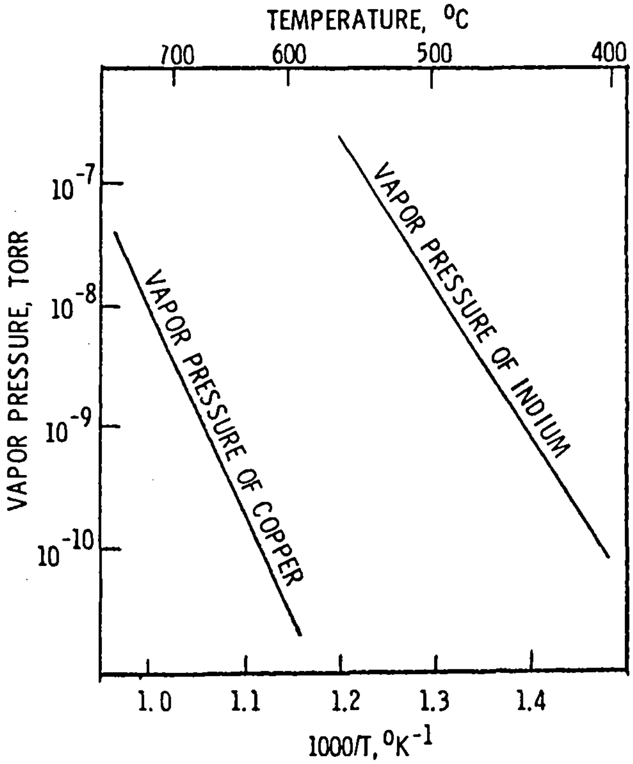

Figure 3-2. Vapor pressure of Cu and In in the temperature range 400°-700°C

most common and reliable technique for the analysis of Cu^{+2} and In^{+3} in solution is the EDTA titration using ethylenediaminetetraacetate and an appropriate indicator.(7) The EDTA titration is based on the formation of metal-EDTA complexes, and the end point in a titration may be ascertained by the use of metal-sensitive indicators. Any metallic species can be determined by the EDTA titration if (1) a method exists to indicate the disappearance of this species, (2) the reaction is stoichiometric, and (3) the reaction is sufficiently rapid. In order to secure a satisfactory titration, the change in the concentration of "free" metal ion must be sufficiently abrupt near the end point. In the case of In^{+3}, a stable complex $[In\text{-}EDTA]^{-1}$ is formed in an acid solution with p_H of about 2. Pyrocatechol violet indicator turns from blue to yellow sharply at the end point. The titration of Cu^{+2} solutiuon is carried out in an alkaline solution by adding p_H 10 ammoniacal buffer until all of the copper is transformed into the tetrammine complex. The murexide indicator produces a distinguishing yellow color, and the end point of EDTA titration is marked by a sharp change to violet. To verify the accuracy of these methods, weighed quantities of In and Cu of better than $99.999^{+}\%$ purity were dissolved in hydrochloric acid and nitric acid, respectively. Aliquots of each solution were then used to determine the concentrations of copper and indium in each solution by the EDTA titration. The results are accurate, on the basis of the weight of Cu and In used, within ±0.5%, and the reproducibility is better than ±0.25%.

While the EDTA titration may be used for the quantitative determination of Cu, In, or the total Cu + In concentration in solutions, no indicators are available for the determination of the individual metal in a mixture of Cu and In solutions. The quantitative analysis of Cu-In solutions was carried by a combination of the EDTA titration (for Cu + In) and spectrophotometric measurements (Cu forms dark blue complexes with several reagents and In does not).

The thermal reduction of Cu and In compounds was carried out in a fused silica reaction tube of 5 cm ID in a resistance-heated tube furnace. The substrates, W/Al_2O_3 or Mo/glass, were of 6 cm^2 in area. As mentioned earlier, the oxides and nitrates are best suited for the deposition of thin films of Cu-In alloys. The oxides are preferred to minimize any side reactions due to the anions. A series of experiments were carred out to investigate the formation of Cu films. In order to deposit a uniform thin Cu film (about 0.5 μm thickness) on the substrate, the copper compound must be applied to the substrate in the form of a solution. CuO and Cu_2O are insoluble in water and cannot be used directly. Since Cu_2O is soluble in aqueous ammonium hydroxide, a weighed quantity of Cu_2O was suspended in water and saturated with ammonia. The solution was filtered, and the concentration of copper in solution determined by the EDTA-titration. A measured volume of the solution required to yield 0.5 μm Cu on a substrate of 6 cm^2 area was applied to the surface of substrates supported on a quartz plate in the reaction tube. Hydrogen purified by diffusion through a palladium-silver alloy was introduced into the reaction tube at 1 ℓ/min. The solution was evaporated by slow heating, and the temperature of the substrate was gradually increased. The formation of Cu on the substrate surface was noted at about 250°C, and the reduction of the Cu compound is essentially complete at 300°C, leaving a uniform Cu film on the substrate surface. The deposited copper was determined by the spectrophotometric technique and found to be within +0.5% of the copper-ammonia solution used. The results are reproducible. Unlike Cu_2O, In_2O_3 is not soluble in common solvents, except mineral acids. However, In_2O_3 appears to form a collodial suspension in the ammonia solution of Cu_2O. A calculated amount of In_2O_3 was added to a known volume of the ammonia solution of Cu_2O to maintain a Cu/In ration of unity. This mixture was placed on a mechanical shaker for several hours. A measured volume of this mixture required to yield 0.5 μm Cu and 1.1 μm In on a substrate surface, placed in a reaction tube with hydrogen flow, and gradually heated to evaporate the solvent. Upon further heating, the Cu compound was found to be reduced at 250°-300°C. However, the indium oxide was considerably more stable and was not reduced at temperatures as high as 500°C. To determine the temperature required for the reduction of In_2O_3, an aqeous suspension of In_2O_3 was placed on the substrate surface in the reaction tube with hydrogen flow. The reaction was carefully monitored during the heating process. When the substrate was held at 510°C for about 30 min, the formation of elemental In was observed. However, the reaction was very slow. A substrate temperature of 550°C was required for the reduction to take place at a reasonable rate. Subsequently, the reduction of the collodial suspension of In_2O_3 in the ammonia solution of Cu_2O was again carried out in a hydrogen flow, and the substrate was heated to 550°C. By optimizing the process parameters, such as the rate of temperature increase and the flow rate of hydrogen, uniform Cu-In alloy films were obtained. However, some deposit was observed on the wall of the reaction tube, indicating the vaporization of some reactant species. The composition of the Cu-In alloy films was then analyzed. The results of several analyses were not in agreement;however, the indium content was lower than expected in all cases. Further, the ammonia solution of Cu_2O was found to be unstable over a period of several days. This approach was discontinued.

Since both $Cu(NO_3)_2$ and $In(NO_3)_3$ are soluble in methanol, mixtures of their solutions with a Cu/In molar ratio of unity was prepared. 0.2 ml of this solution can yield 0.5 μm Cu and 1.1 μm In on a substrate of 6 cm^2 area. After the drying of the solution, the substrate was maintained at 250°-300°C in a hydrogen atmosphere for a few minutes. Under these conditions, the nitrates are decomposed into the oxides, and copper oxide is reduced to Cu. By further increasing the temperature to 550°C, indium oxide is reduced to the elements, yielding a uniform, adherent Cu-In film on the substrate. The spectrophotometric analysis and EDTA titration have shown that all Cu-In films are In-deficient. This is due to the vaporization of In_2O_3 or In. On the basis of these results, it has been established empirically that by using a In/Cu molar ration of 1.06 in the reactant mixture, nearly stoichiometric Cu-In alloys can be obtained.

3.2 PREPARATION AND PROPERTIES OF $CuInSe_2$ FILMS

The heating of nearly stoichiometric Cu-In films in a H_2 + H_2Se atmosphere was used for the preparation of $CuInSe_2$ films. The important process parameters are the substrate temperature, the flow rate of the selenizing agent (a 90% H_2 - 10% H_2Se mixture), and the duration of selenization. The temperature of the Cu-In film during selenization is important in determining the grain structure in resulting films. The use of selenization temperatures of 630°C (the melting point of 1:1 Cu-In alloy) or above involve gas-liquid reaction and yields large-grain films, while that at lower temperatures involves gas-solid reactions and yields small-grain films. The use of high selenization temperature requires relatively thick Cu-In films, 10 μm or more, in order to achieve uniform wetting of the substrate surface by the liquid Cu-In films, and therefore uniform $CuInSe_2$ films. Further, brownish-black films always deposited on the wall of the reaction tube. Microchemical analysis indicated that these films consisted mainly of indium selenide and a considerably less amount of copper selenide. Thus, a lower substrate temperature must be used. At temperatures below 500°C, relatively thin Cu-In films, 2 μm for example, are more suitable. The selenization of Cu-In films was carried out in-situ immediately following the deposition of Cu-In alloys using an H_2-H_2Se mixture. Since indium tends to form volatile selenides, the reaction tube was filled with the selenizing agent before heating, and the flow rate of the selenizing agent was reduced to about 20 ml/min. during the heat treatment. The composition of $CuInSe_2$ films was found to depend strongly on the substrate temperature. The Cu/In ratio in the selenized films increases as the selenization temperature increases, indicating the more pronounced loss of In during the selenization process. The loss of In is appreciable at 400°-500°C. For example, when a nearly stoichiometric Cu-In film was selenized at 500°C for one hour, the resulting film consisted of 36.4% Cu, 15.6% In, and 48% Se. The pronounced loss of In during selenization at 400°-500°C has been demonstrated in many experiments.

Thus, an In-rich Cu-In alloy must be used for the selenization process in order to obtain nearly stoichiometric films. For example, when a Cu-In alloy containing 43 ±3% Cu and 57 ±5% In was selenized at 400°C for one hour, the resulting film contained 24.5 ±1.4% Cu, 23.5 ±1.4% In, and 52 ±3%Se. Similar results were obtained for H_2 - H_2Se flow rates of 10-30 ml/min. and selenization times of 30-100 min. The deposited films showed x-ray diffraction peaks in agreement with those reported for $CuInSe_2$ in the literature. The as-grown surface of a $CuInSe_2$ film is shown in Figure 3-3.

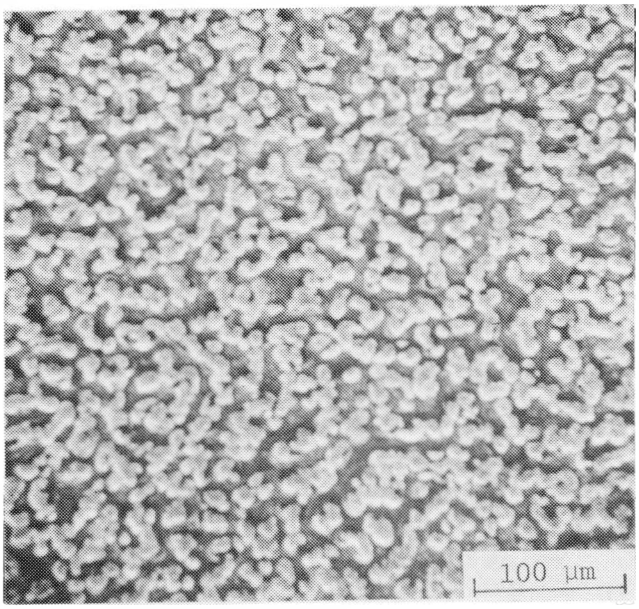

Figure 3-3. As-grown surface of a $CuInSe_2$ film on a W/glass substrate

An alternative approach was used to minimize the effects of the high volatility of indium sulfides. A known volume of $In(NO_3)_3$ solution was applied to the substrate surface, thermally decomposed to In_2O_3 which was converted to In_2Se_3 by treating with a H_2-H_2Se mixture. The conversion yield of $In(NO_3)_3$ to In_2Se_3 was determined to be 83-84%, i.e., 1 mg of $In(NO_3)_3$ is converted to 1.3 mg of In_2Se_3. Subsequently, an equivalent amount of $Cu(NO_3)_2$ solution was added to In_2Se_3, heated in a hydrogen atmosphere and again selenized with a H_2-H_2Se mixture at 300°C. Although the resulting films have been found to be essentially stoichiometric, pinholes were frequently present.

While nearly stoichiometric $CuInSe_2$ films have been prepared by the selenization of Cu-In films deposited by the thermal reduction of Cu and In compounds, two major problems were uncovered: composition inhomogeneities and irreproducible resistivity. These problems can probably be alleviated by refining the process parameters; however, the limited time remaining in this program did not permit any further investigations. Several solar cells of 1 cm^2 area were made by evaporating 0.3 - 0.5 μm of CdS onto the surface of $CuInSe_2$ films. They showed only very weak photoresponse. (V_{oc} of a few mV and I_{sc} of less than 2 mA/cm^2), due presumably to the inhomogeneity and resistivity problems associated with the $CuInSe_2$ films.

SECTION 4.0

$CuInSe_2$ FILMS BY SELENIZATION OF ELECTRO-DEPOSITED Cu-In FILMS

Electroplating is a common technique for the deposition of metal films on conducting substrates. The deposition techniques of Cu and In films by electroplating are well established. The deposition of $CuInSe_2$ films by the selenization of electrodeposited Cu-In films has been explored in this program.

4.1 ELECTRODEPOSITION OF Cu AND In FILMS

Copper or indium may be deposited from several electrolytes using a copper or indium anode. The most commonly used electrolytic solutions for the deposition of Cu and In are summarized in Tables 4.1 and 4.2, respectively. A comparison of the relative merits of various electrolytes, such as contaminations by electrolyte inclusion, ease of reproducibility, and efficiency of plating, suggests that acid solutions of copper sulfate and indium sulfamate are best suited for the electrodeposition of Cu-In films on conducting substrates. While it is preferred to electroplate indium first because of its good wettability to the substrates, copper must be plated first due to the higher electropositivity of indium. Indium film would be partially dissolved upon immersion in the copper-plating solution.

The commonly recognized parameters of the electroplating process are: temperature, current density, and agitation. Their effects on a plating operation are interrelated. Increasing temperature and agitation usually enables one to obtain higher current efficiencies and to use higher current densities. It is a good practice to operate at the highest possible temperature and current density consistnt with the limitations imposed by the quality of deposit required. Agitation may be carried out by cathode movement, solution movement, or both, and any agitation should be as uniformly distributed as possible to avoid nonuniformities in the structure and thickness of the deposit.

The electroplating of Cu and In films for conversion into $CuInSe_2$ differs from most conventional industrial plating in that the Cu and In films must be of controlled and uniform thickness. The uniformity of electroplated metal films is determined by the local current density at each portion of the surface and by the cathode efficiency at that current density. The local current density is determined by the primary current distribution and the local polarization. The primary current distribution is determined completely by the geometry of the plating cell. The term polarization combines all physical and electrochemical phenomena which operate to change the properties of the solution in the vicinity of the electrode. These changes result in an actual local or "secondary" current distribution which differs from the primary distribution. The current distribution over an electrode in the absence of polarization and other disturbing factors at the electrode is referred to as the primary current distribution. It is

Plating Solution	P_H	Temp., ^oC	Current Density mA/cm^2	Cathode Efficiency, %
$Cu(BF_4)_2$ and HBF_4 (60g Cu/ℓ)	0.8-1.5	30-80	80-140	95-100
CuCN + NaCN + NaOH (53g Cu/ℓ + 10g CN^-/ℓ)	12	60-80	10-100	99+
$CuSO_4 \cdot 5H_2O + H_2SO_4$ (50g Cu/ℓ + 30-80g H_2SO_4/ℓ)		30-45	25-110	95-100

Table 4-1. **Electrodeposition of Copper**

Plating Solution	P_H	Temp., ^oC	Current Density mA/cm^2	Cathode Efficiency %
Indium sulfamate (100 g/ℓ) + soldium sulfamate (150 g/ℓ) + sulfamic acid (25 g/ℓ) + NaCl	1.5-2	RT	10-20	90
In + KCN + KOH + Dextrose (65g In/ℓ + 180g KCN/ℓ)	13	RT	15-20	50-75
$In(BF_4)_3$ (250 g/ℓ) + H_3BO_3 (30g/ℓ) + NH_4BF_4 (40 g/ℓ)	1.0	20-35	50-100	40-75
$In_2(SO_4)_3$ (20 g/ℓ) + Na_2SO_4 (10 g/ℓ)	2.0-2.5	RT	20-45	30-70

Table 4-2. **Electrodeposition of Indium**

determined entirely by the geometry of the system, including the shape and size of the electrodes and their conductivity. Whenever a voltage is applied between two electrodes in an electrolyte, every point in the electrolyte assumes some potential intermediate between that of the two electrodes. Since the conductivity of the metal electrodes is several million times that of the electrolyte, every point on the electrode may be asumed to be at the same potential. Similarly, equipotential surface will be found in the electrolyte surrounding each electrode. Close to one electrode, the equipotential surface resembles that electrode in shape; however, the shape changes as one moves farther away until at last the equipotential surface close to the second electrode assumes a shape more or less conforming to that electrode. This is shown schematically in Figure 4.1. The current density is the greatest where the equipotential lines are crowded most closely together. On the basis of these considerations, three possible arrangements

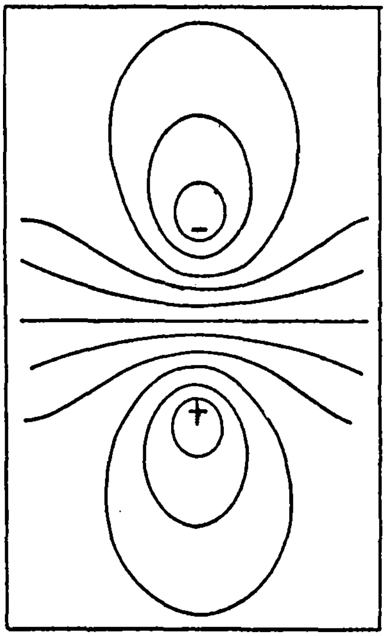

Figure 4-1. Equipotential surfaces in an electrolyte with two metal electrodes

providing perfectly uniform current distribution may be deduced: infinite parallel planes, infinite concentric cylinders, and concentric spheres. It can be shown that any surface of current flow may be replaced by an insulating boundary and that any equipotential surface may be replaced with an electrode. Thus, the infinite parallel planes may be boxed in with three perpendicular insulating walls and an air surface, and the walls must be exactly perpendicular to the electrodes. One example would be a plating rack full of closely spaced flat parts, equidistant between two rows of anodes, in a tank just big enough to hold the rack. The electrolytic cell used for the plating of Cu and In was constructed on the basis of this principle.

To determine the plating efficiency, copper was plated onto W/Al_2O_3 and Mo/Corning 7059 glass substrates from an acid solution of copper sulfate, at room temperature and at a current density of 40 mA/cm^2, using a Cu anode. The plated Cu was dissolved in diluted nitric acid, neutralized, and titrated with EDTA. The plating efficiency of Cu was determined to be 99%. Indium was plated from an acid solution of indium sulfamate at a current density of 20 mA/cm^2, using an indium anode. The plated metal was dissolved in diluted hydrochloric acid, neutralized with ammonium hydroxide to a p_H of 2.5, and titrated with EDTA. The plating efficiency of In was determined to be 98%. The successive plating of Cu and In on substrates was also carried out, and the analysis of Cu and In in the resulting films by EDTA titration and spectrophotometric determination yielded similar plating efficiencies. Because of the relatively high current density required for the deposition of uniform films, the time required to obtain 0.5 μm of Cu and 1.1 μm of In (required for 5 μm $CuInSe_2$) are very short, and special precautions must be taken to control the time of deposition. Many electroplating experiments have been carried out, and the Cu/In molar ratio can be controlled within +2%.

4.2 PREPARATION AND PROPERTIES OF $CuInSe_2$ FILMS

The procedure used for the selenization of electroplated Cu-In films into $CuInSe_2$ films was similar to that of chemically deposited Cu-In films. Since indium selenides are more volitile than copper selenides, In-rich Cu-In films were used. The specimens were placed in a fused silica reaction tube of 5 cm ID in a resistance-heated furnace, heated in a hydrogen atmosphere at 300°-400°C to enhance the interdiffusion of Cu and In. The temperature was reduced to 150°-200°C, and the reaction tube purged with a 90% H_2 - 10% H_2Se mixture (low temperature was used to minimize the loss of indium selenides). The flow rate of the H_2-H_2Se mixture was then reduced to about 15-20 ml/min, and the specimens were selenized at 300°-500°C for 10-30 minutes.

In order to obtain pinhole-free $CuInSe_2$ films, the thickness of Cu and In films must not be less than 0.25 and 0.55 μm, respectively. In a series of experiments, the thickness of Cu film was maintained at 0.5 μm and that of In varied from 1.24 to 1.34 μm (1.1 μm for stoichiometric Cu-In). The selenization was carried out at 400°C, and the composition of the resulting $CuInSe_2$ was analyzed by the electron microprobe technique at SERI. The results are shown in Table 4-3. It is apparent that In-rich Cu-In films are required for stoichiometric $CuInSe_2$ films, particularly at higher selenization temperatures. However, the processing techniques must be improved for better control of the composition of $CuInSe_2$ films.

The $CuInSe_2$ films are polycrystalline with an average grain size of 4-5 μm. Figure 4-2 shows the as-grown surface of a typical film. Many heterojunction solar cells of about 1 cm^2 area were prepared by evaporating 0.3-0.5 μm of cadmium sulfide onto the surface of $CuInSe_2$ films. Under simulated AM1 conditions using tungsten-halogen lamps, the highest open-circuit voltage was 0.35 V, and the highest short-circuit current density was 24 mA/cm^2. The best solar cell has an open-circuit voltage of 0.31 V, a short-circuit current density of 19 mA/cm^2, and a fill factor of 51%, corresponding to a

Substrate	Thickness of Cu, μm	Thickness of In, μm	Duration of Selenization, minutes	Film Composition, at %		
				Cu	In	Se
W/Al_2O_3	0.5	1.34	20	22.6±2.6	24.6±2.6	52.8±6.0
Mo/glass	0.5	1.34	30	22.9±1.7	24.6±1.9	52.5±5.0
W/Al_2O_3	0.5	1.32	15	24.1±1.4	24.7±1.4	51.3±2.9
Mo/glass	0.5	1.24	15	24.1±1.4	23.4±1.4	52.5±3.1
W/Al_2O_3	0.5	1.24	15	24.6±1.4	23.5±1.3	52.0±3.0

Table 4-3. Composition of $CuInSe_2$ Films by the Selenization of Electrodeposited Cu-In on W/Al_2O_3 and Mo/glass Substrates

conversion efficiency of about 3%. It is believed that this conversion efficiency can be significantly improved by optimizing the processing techniques.

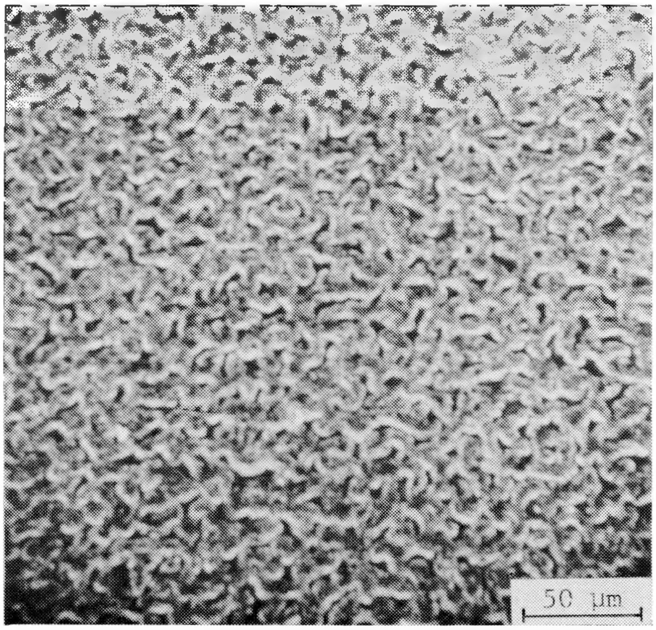

Figure 4-2. **As-grown surface of a $CuInSe_2$ film on a Mo/glass substrate**

SECTION 5.0

CONCLUSION

Three non-vacuum techniques have been investigated for the deposition of solar cell quality $CuInSe_2$ films on foreign substrates: (1) the close-spaced chemical vapor transport (CSCVT) technique, (2) the formation of a Cu-In alloy film by chemical reduction followed by selenization, and (3) the formation of a Cu-In alloy film by electroplating followed by selenization.

A detailed investigation of the CSCVT technique indicated that $CuInSe_2$ films with good compositional and structural properties can be obtained; however, the photovoltaic characteristics are presumably degraded by the inclusion of iodine and other impurities.

The deposition of Cu-In films by the chemical reduction technique is simple in principle; however, indium compounds are considrably more stable than copper compounds, resulting in inhomogenous composition of the alloy. Further, indium selenides are volatile at temperatures as low as 400°C, and In-rich Cu-In alloy must be used in order to obtain stoichiometric $CuInSe_2$ films.

The most important parameter of the electroplating of Cu and In films of controlled thickness and uniformity is the geometry of the system, including the shape and size of their electrodes and their conductivity. By optimizing the geometrty of the plating system, the Cu/In molar ratio can be accurately controlled. However, the selenization process is more critical due to the higher volatility of indium selenide than copper selenides. While the best solar cell of 1 cm^2 area prepared in this work has an AM1 efficiency of only about 3%, this technique is believed to be most promising among the three non-vacuum techniques investigated.

SECTION 6.0

REFERENCES

(1) F.H. Nicoll, "The Use of Close-Spacing in Chemical Transport Systems for Growing Epitaxial Layers of Semiconductors," J. Electrochem. Soc., 110, 1165 (1963).

(2) H. Haupt and K. Hess, "Growth of Large $CuInSe_2$ Single Crystals," in "Third International Conference on Ternary Compounds," Inst. Phys. Conf. Ser. No. 35, p. 5 (1977).

(3) J. Parkes, R.D. Tomlinson, and M.J. Hampshire, "Crystal Data for $CuInSe_2$," J. Appl. Cryst., 6, 414 (1973).

(4) R.A. Mickelson and W.S. Chen, "Development of a 9.4% Efficient Thin-Film $CuInSe_2$/CdS Solar Cell," Proceedings of the 15th IEEE Photovoltaic Specialist Conference, Orlando, FL (IEEE, New York, 1981), pp. 800-804.

(5) M. Hansen, "Constitution of Binary Alloys," p. 591, McGraw-Hill Book Co., New York (1958).

(6) D.D. Wagman, et. al., "Journal of Physical and Chemical Reference Data," Vol. II, Supplement No. 2 (1982).

(7) C.L. Wilson and D.W. Wilson, "Comprehensive Analytical Chemistry," Vol. IB, p. 288, Elsevier Publishing Co., New York (1960).

Document Control Page	1. SERI Report No. SERI/STR-211-3123	2. NTIS Accession No.	3. Recipient's Accession No.

4. Title and Subtitle
Deposition of Copper Indium Diselenide Films by Low-Cost Techniques, Final Subcontract Report, 15 November 1983 - 14 September 1985

5. Publication Date
February 1987

6.

7. Author(s)
Poly Solar Incorporated

8. Performing Organization Rept. No

9. Performing Organization Name and Address
Poly Solar Incorporated
Garland, Texas 75041

10. Project/Task/Work Unit No.
3494.10

11. Contract (C) or Grant (G) No.
(C) XL-4-03125-1
(G)

12. Sponsoring Organization Name and Address
Solar Energy Research Institute
A Division of Midwest Research Institute
1617 Cole Boulevard
Golden, Colorado 80401-3393

13. Type of Report & Period Covered
Technical Report

14.

15. Supplementary Notes
Technical Monitor: H. S. Ullal

16. Abstract (Limit: 200 words) This is the final technical report of a research program on copper indium diselenide films. The objectives of this program were to prepare device-quality, thin-film, polycrystalline CuInSe$_2$ by low-cost techniques and to produce heterojunction solar cells 1 cm^2 in area with an AM 1 efficiency of 8% or higher. In this work, three approaches were used to deposit p-type CuInSe$_2$ films: close-spaced chemical vapor transport (CSCVT), thermal reduction of Cu and In compounds followed by selenization, and electroplating of Cu and In films followed by selenization. The important process parameters for (1) depositing CuInSe$_2$ films by the CSCVT technique, (2) depositing Cu-In films by chemical reduction and electroplating, and (3) forming CuInSe$_2$ films by the selenization of Cu-In films were investigated. Many p-CuInSe$_2$ films were deposited on conducting and insulating substrates, and their properties characterized. Heterojunction solar cells were fabricated from p-CuInSe$_2$ films prepared by the three techniques, and their photovoltaic characteristics evaluated. The procedures and results are summarized.

17. Document Analysis
a. Descriptors Photovoltaic cells ; copper indium selenide solar cells ; thin films ; deposition

b. Identifiers/Open-Ended Terms

c. UC Categories
63

18. Availability Statement
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

19. No. of Pages
34

20. Price
A03

Form No. 0069 (3-25-82)