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Chemical Vapor Deposited Copper Indium Diselenide Thin Film Materials Research

Final Report
15 November 1982 – 14 January 1984

A Subcontract Report

Poly Solar Incorporated
Garland, Texas

Prepared under Subcontract No. XL-3-02208-01

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

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Summary

This is the Final Technical Report of a research program "Chemical Vapor Deposited Copper Indium Diselenide Thin Film Materials Research" supported by the Solar Energy Research Institute under Subcontract No. CL-3-02208-01. The objective of this contract is to demonstrate the feasibility of producing device quality copper indium diselenide films by the close-spacing chemical vapor transport (CSCVT) technique.

The technical approaches used in this work consist of (1) the preparation of the $CuInSe_2$ source material by direct synthesis and the characterization of its properties, (2) the deposition of $CuInSe_2$ films on conducting and insulating substrates by the CSCVT technique, and (3) the formation and characterization of heterojunction solar cells.

During the course of this subcontract, a number of copper indium selenide ingots (source material) have been synthesized from the elements, and their structural and electrical properties characterized. The deposition of p-type $CuInSe_2$ films on graphite, alumina, and coated graphite substrates by the CSCVT technique using iodine and hydrogen iodide as the transport agent has been carried out under a wide range of conditions. The compositional, structural, and electrical properties of $CuInSe_2$ films have been characterized. A number of n-ZnO/p-$CuInSe_2$ and n-CdO/p-$CuInSe_2$ heterojunction solar cells have been prepared by the deposition of the transparent oxide on p-$CuInSe_2$ films by ion-beam sputtering. The AM1 efficiency of these cells is in the range of 2-3%. The low efficiency is believed, at least in part, to the damage of the p-$CuInSe_2$ film by the ion-beam. The vacuum evaporator for the deposition of CdS films is now in operation, and CdS films will be used as the window material in the future work.

I. Introduction

This is the Final Technical Report of a research program "Chemical Vapor Deposited Copper Indium Diselenide Thin Film Material Research" supported by the Solar Energy Research Institute under Subcontract No. XL-3-02208-01. The objective of this contract is to demonstrate the feasibility of producing device-quality copper indium diselenide films by the close space chemical vapor transport (CSCVT) technique.

Copper indium diselenide, a direct gap semiconductor with a room temperature band gap of about 1 eV, has very large optical absorption coefficient at the band edge and beyond,(1) and the minority carrier diffusion length becomes relatively unimportant in the operation of photovoltaic devices. Thus, $CuInSe_2$ is particularly suited for thin film devices.

Copper indium selenide crystallizes in the chalcopyrite structure with lattice parameters $a = 5.78\mathring{A}$ and $c = 11.62\mathring{A}$, and large crystals have been grown by the directional solidification of the melt of a stoichiometric mixture of the constituent elements.(2,3) Since the first report of a single crystalline heterojunction device of the configuration p-$CuInSe_2$/n-CdS (prepared by the evaporation of cadmium sulfide onto single crystalline copper indium selenide) with a conversion efficiency of 12%,(4) considerable efforts have been directed to the fabrication and characterization of thin film devices of the same configuration. The deposition of $CuInSe_2$ films on foreign substrates was carried out, in most cases, by vacuum techniques, such as evaporation and sputtering. Thin film $CuInSe_2$/CdS heterojunction solar cells with AM1 efficiencies of 4-5%

were first reported by Kazmerski et al. in 1976.$^{(5)}$ Better control of the copper and indium fluxes at the substrate surface has improved the stoichiometry of $CuInSe_2$ films, leading to the development of thin film cells of nearly 10% conversion efficiency.$^{(6)}$ By using a solid solution of cadmium sulfide and zinc sulfide as the window layer, heterojunction solar cells with an AM1 efficiency of 10.9% have recently been produced.$^{(7)}$ The use of spray pyrolysis for the preparation of n-ZnO/p-$CuInSe_2$ solar cells with an AM1 efficiency of about 2% has been reported recently.$^{(8)}$ The vacuum techniques have been the major technique used for the deposition of p-$CuInSe_2$ films. The vacuum techniques yield, in general, films consisting of relatively small grains, about 1 µm, as compared with films deposited by chemical vapor deposition techniques. The chemical vapor deposition of $CuInSe_2$ films should satisfy at least two requirements: (1) the formation of elemental copper and indium should take place on the surface of the substrate in order to obtain adherent deposit, and (2) the deposition rate of copper must be similar to that of indium in order to maintain the stoichiometry of the film. The deposition of $CuInSe_2$ films by the reaction of gaseous inorganic compounds in a gas flow system is relatively difficult. While the deposition of indium by the disproportionation of indium monochloride (formed by the reaction of indium and hydrogen chloride) at 600°-700°C is well established, copper cannot be readily codeposited with indium. The volatile copper compounds, such as the halides, are readily reduced by hydrogen in the gas phase before reaching the substrate surface, and elemental copper has no appreciable vapor pressure at the deposition temperature (about 10^{-8}Torr at 700°C). On the other hand, single crystalline platelets of $CuInSe_2$ have been grown by the chemical vapor transport technique using iodine as a transport agent in a sealed tube.(9) Thus, the chemical transport technique appears to be feasible for the deposition of $CuInSe_2$ films. In this program, the close-spacing chemical vapor transport (CSCVT) technique has been used for the deposition of $CuInSe_2$ films on foreign substrates; the CSCVT technique is essentially diffusion-limited and has the advantages that all components of the source material are directly transported to the substrate surface independent of the conditions elsewhere in the system. The technical approaches used in this program consist of (1) the preparation of $CuInSe_2$ source material by direct synthesis and the characterization of its properties, (2) the deposition of $CuInSe_2$ films on conducting and insulating substrates by CSCVT and the characterization of their properties, (3) the formation and characterization of heterojunction solar cells.

During the course of this subcontract, an apparatus for the deposition of $CuInSe_2$ films by the CSCVT technique has been designed and constructed. Many $CuInSe_2$ ingots of different compositions have been synthesized and characterized and used as the source material for the CSCVT. A number of $CuInSe_2$ films have been deposited on conducting and insulating substrates, and their compositional, structural, and electrical characterization carried out. These films were used for the fabrication of n-ZnO/p-$CuInSe_2$ and n-CdO/p-$CuInSe_2$ heterojunction solar cells. The procedures and results are summarized in the following sections.

II. Technical Discussion

II.1 Preparation of CuInSe2 Source Material

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 fused silica tube of rectangular cross-section, 2.5 cm x 1.5 cm. Weighted 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. In these experiments, the Cu/In molar ratio was maintained at unity and the amount of selenium was varied from 0.3% deficient to 0.6% excess. The fused silica tube was heated in a resistance-heated furnace at 1100°C and quenched to room temperature. The size of the ingot was usually 15 cm long, 2.5 cm wide, and 3-5 mm thick.

The $CuInSe_2$ ingots were single-phase, large grain (several millimeters and larger), polycrystalline; an example of the as-solidified surface is shown in Fig. 1. The $CuInSe_2$ ingots, analyzed through the courtesy of Mr. Chuck Herrington at SERI using the electron microprobe technique, are essentially stoichiometric. The typical atomic percentages of Cu, In, and Se are 24.50-24.55%, 25.67-26.11, and 49.83-48.35, respectively. The conductivity type and electrical resistivity of the ingot depend on the selenium content in the reaction mixture. Selenium deficiency in the reactant yields n-type $CuInSe_2$ while selenium excess yields p-type material, and the resistivity of the p-type material decreased with increasing selenium concentration. The effect of selenium concentration in the reaction mixture on the conductivity type and electrical resistivity of the polycrystalline ingot is shown in Fig. 2.

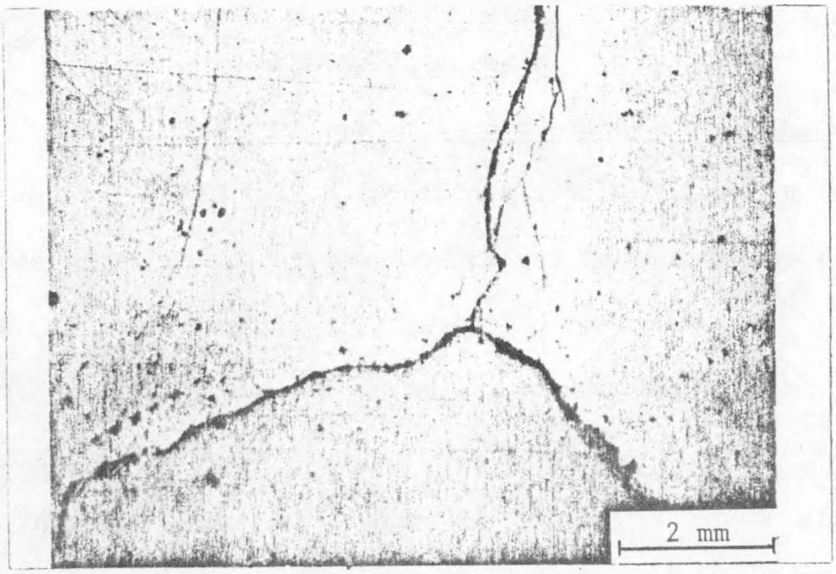

Fig. 1 Surface of a $CuInSe_2$ ingot prepared by the combination of the elements in a sealed tube.

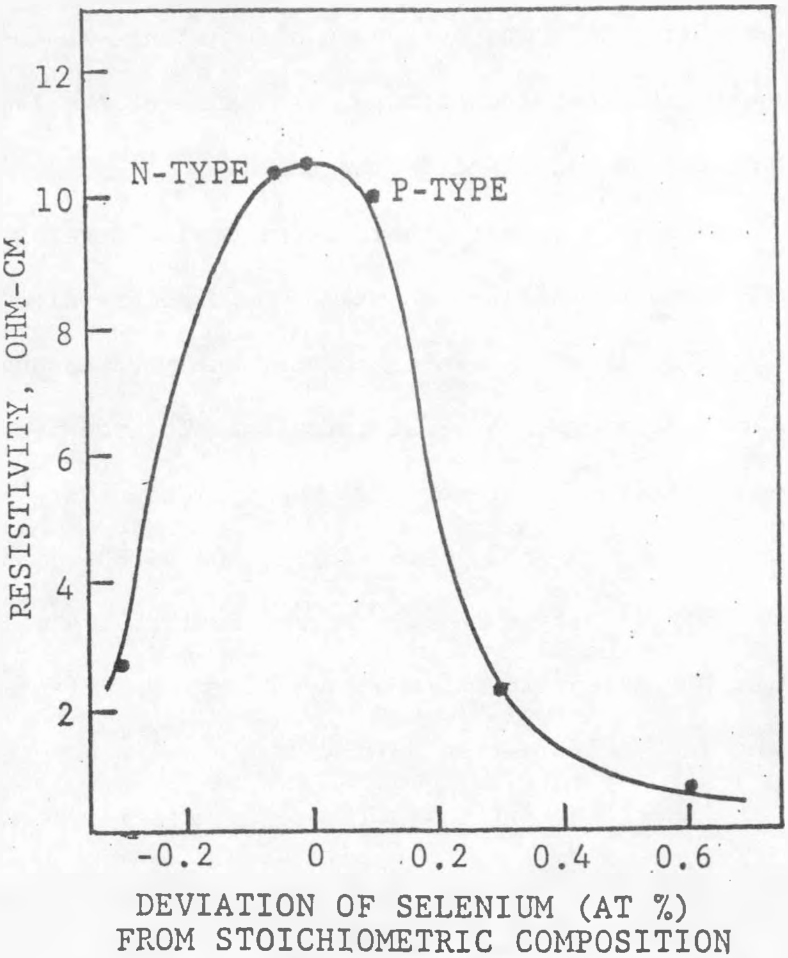

Fig. 2 Effect of selenium concentration in the reaction mixture on the conductivity type and electrical resistivity of synthesized $CuInSe_2$ ingots.

The photovoltaic properties of $CuInSe_2$ ingots were demonstrated by using the n-ZnO/p-$CuInSe_2$ heterojunction structure. About 0.1 μm of a ZnO film was deposited on a p-type $CuInSe_2$ ingot by ion-beam sputtering. The V_{oc} of the resulting structure under the AM1 condition varied between 100 and 200 mV. After heating in oxygen at 200°C for 1 hr, the V_{oc} increased to 300-350 mV and was also more uniform over the entire specimen. n-ITO/p-$CuInSe_2$ structures were also prepared. Their open-circuit voltages were similar to those of n-ZnO/p-$CuInSe_2$ structures; however, they degraded after heating in oxygen.

II.2 Deposition of $CuInSe_2$ Films by CSCVT

The chemical transport technique has been widely used for the crystal growth and film deposition of many electronic materials.(10) The chemical transport technique is applicable to solid state materials which react reversibly with a gaseous reagent (the transport agent) to form volatile products. Since the equilibrium constant of the chemical reactions is, in general, temperature dependent, the transport can then be brought about by the presence of a temperature gradient. The direction of the transport in the temperature gradient depends on the variation of the equilibrium constant with temperature. When the equilibrium is shifted toward the formation of the solid as the temperature is decreased, the solid is transported from a high temperature zone to a lower temperature region. The chemical transport process can usually be achieved at temperatures considerably below the melting point of the transported material. For example, cadmium sulfide reacts reversibly with iodine according to the following equation:

$$CdS(s) + I_2(g) = CdI_2(g) + S(g)$$

and the chemical equilibrium of this reaction shifts to the left at lower temperatures. Thus, iodine may be used to transport cadmium sulfide source material from a high temperature zone, 500°C for example, to a substrate surface at a lower temperature, about 400°C. In addition to binary compounds, crystals of ternary and quarternary compounds, such as $CuInS_2$, $CuInSe_2$, $CuA\ell Se_2$, $CuGaS_2$, Cu_2ZnGeS_4, Cu_2CdSiS_4, etc., have also been grown by chemical transport using iodine as a transport agent.(11-14)

The chemical transport technique may be carried out in a closed tube or in a gas flow system. In the former, the transport agent recycles between the source zone and the substrate zone, and essentially equilibrium conditions are established. In the gas flow system, a relatively high reaction rate between the source material and transport agent is essential, and the transport agent is not re-used. In addition, the close-spacing chemical vapor transport (CSCVT) technique is of particular interest.(15) In this method, the source and substrate are separated by only a fraction of a millimeter. If the spacing is less than about 10% of the diameter of the source and substrate, then the chemical transport conditions in between are largely independent of conditions elsewhere in the system. This is the case because the transport agent is not consumed in transporting material and is therefore available between the source and substrate for continued re-use. Close-spacing of source and substrate also provides direct transport of each component of the material across the space. This is especially advantageous for compounds of elements with widely different properties. The source material is utilized efficiently.

The apparatus used for the CSCVT technique must be pressure tight, inert to the transport agent, and able to provide the necessary temperature gradient. Although horizontal reactors using infrared heaters are widely used for CSCVT, (15) these reactors are only suitable for small samples, say 1 cm^2. Resistance-heated furnaces must be used for larger samples, say 10 cm^2, to maintain temperature uniformity. Both horizontal and vertical reactors have been constructed for the deposition of $CuInSe_2$ films by the CSCVT technique using iodine and hydrogen iodide as the transport agent. However, the major portion of the transport experiment was carried out in the vertical reactor, as shown in Fig. 3, for ease of operation During the early stage of this work, graphite heaters were used to maintain the source material and the substrate at the desired temperature. However, the graphite heaters were found to be too porous, even after coating with silicon carbide. Silicon heaters, inert to the transport agents at the temperatures used, have been used in recent work with much improved results. Quartz rods of 1 mm diameter were used as spacers between the source material and the substrate. The entire assembly was enclosed in a fused silica tube of 55 mm ID 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, and the pressure of iodine or hydrogen iodide, the transport agent. Many CSCVT experiments were carried out to determine the range of process parameters required for the deposition of uniform $CuInSe_2$ films.

Both insulating substrates, alumina (Coors ADS 99.5), and conducting substrates, graphite, coated graphite, and coated alumina, were used for

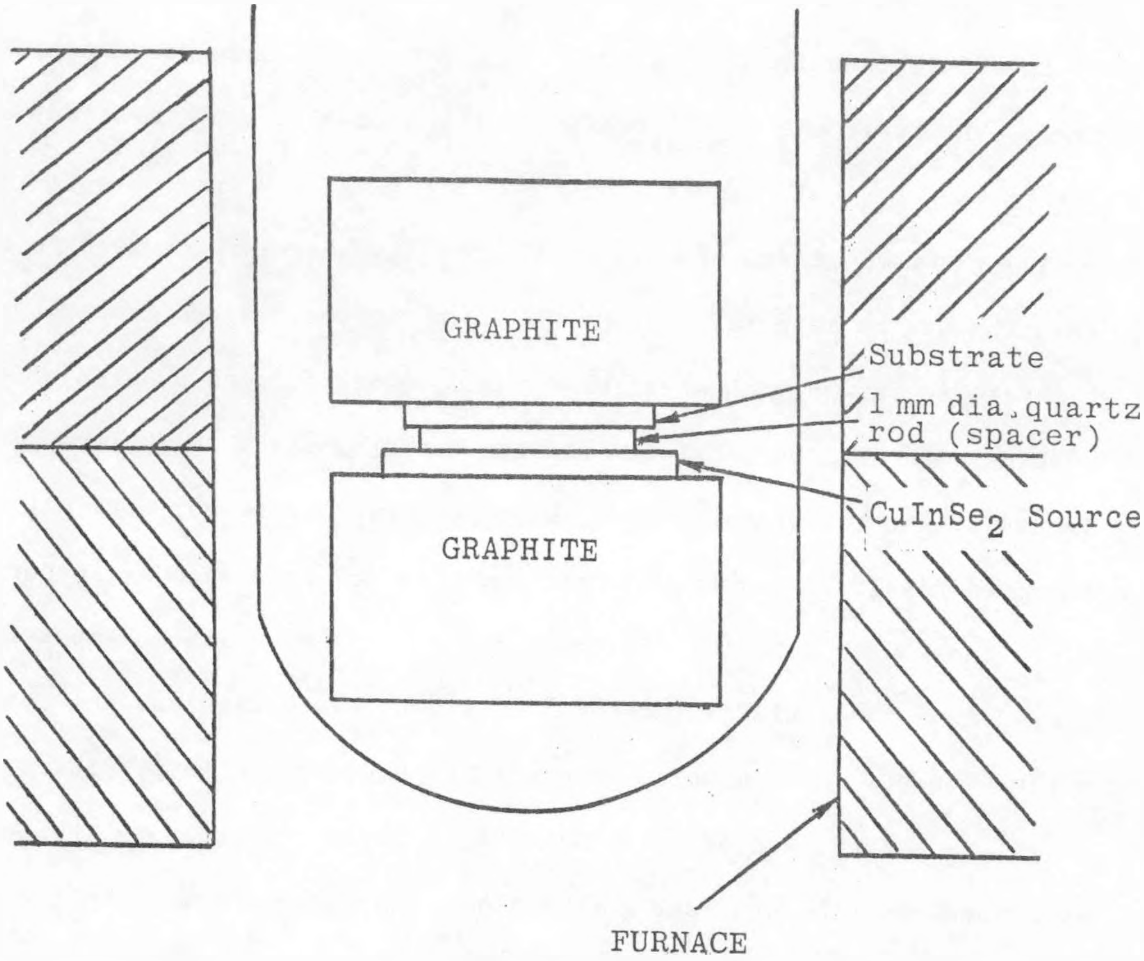

Figure 3. Schematic diagram of the apparatus for the deposition of CuInSe$_2$ films by the CSCVT technique.

the deposition of $CuInSe_2$ films. Because of its porosity, 15-25%, the surface of graphite substrates has a high concentration of pits which appear to interfere with the nucleation of $CuInSe_2$. Tungsten-coated graphite is unsuitable as a substrate because of the reactivity of tungsten toward iodine or hydrogen iodide, the transport agent, at high temperatures. To minimize the pinhole problems, the substrate surface was coated with a thin layer (1-2 μm) of carbon by the pyrolysis of propane at 1100°C or with a thin layer of silicon carbide by the pyrolysis of dimethyldichlorosilane. Both carbon-coated and silicon carbide-coated graphite substrates have provided uniform $CuInSe_2$ films.

The source temperature is important in that it determines the reaction rate between the source material and iodine, and source temperatures in the range of 400°-700° were used. At low source temperatures, such as 400°C, the reaction rate is too low to obtain any reasonable rates of deposition. At too high temperatures, such as 700°C, the selenium dissociation pressure becomes appreciable and the deposited films were selenium deficient (high resistivity p-type or n-type). The substrate temperature determines the rate of nucleation and deposition of $CuInSe_2$ films; the nucleation rate decreases with increasing substrate temperature. To simplify the investigation of the process parameters, the source-substrate separation was fixed at 0.1 cm, and the source-substrate temperature difference was fixed at 20°C. The partial pressure of the transport agent was in the range of 100-200 Torr, and the substrate temperature was in the range of 500°-620°C.

II.3 Properties of $CuInSe_2$ Films

The microstructure of $CuInSe_2$ films depends strongly on the substrate temperature and the partial pressure of the transport agent. At low substrate temperatures, such as 450°C, and low pressures of transport agents, the grains are loosely packed and continuous films cannot be obtained. Films of improved microstructure were obtained at higher temperatures, 520°C or above, and at higher iodine pressures. As an example, Fig. 4 shows the scanning electron micrographs of $CuInSe_2$ films deposited on graphite substrates at 450°C with low iodine pressure and at 520°C with high iodine pressure. Further, under the same deposition conditions, the nucleation and growth of $CuInSe_2$ are also affected by the nature of the substrate. For example, the nucleation of $CuInSe_2$ takes place more readily on alumina than on graphite, as shown in Fig. 5. Also, the growth of $CuInSe_2$ films on alumina at 600°C is frequently columnar (Fig. 6) while those grown at lower temperatures are usually random. The columnar material also shows the most dense packing of crystallites.

In most cases, the deposit consists of crystallites of 5-10 μm size. The composition of the deposited films was analyzed through the courtesy of Mr. Chuck Herrington by the electron microprobe technique, and the results are summarized in Table I. In both films, the In/Cu molar ratio appears to be slightly greater than unity due possibly to the relatively low source temperature.

Table I. Composition of CSCVT $CuInSe_2$ Films by Microprobe Analysis

Substrate	Cu, at %	In, at %	Se, at %
Graphite	24.33 ± 0.85	26.49 ± 0.92	49.17 ± 1.72
Alumina	24.86 ± 0.5	26.13 ± 0.52	49.01 ± 0.98

The crystallographic properties of the $CuInSe_2$ films deposited on graphite substrates by the CSCVT technique have been determined by the

Fig. 4 Scanning electron micrographs of $CuInSe_2$ films on graphite substrates deposited at 450°C (upper) and 520°C (lower).

Fig. 5 Scanning electron micrographs of $CuInSe_2$ films deposited on silicon carbide-coated graphite (upper) and alumina substrates (lower).

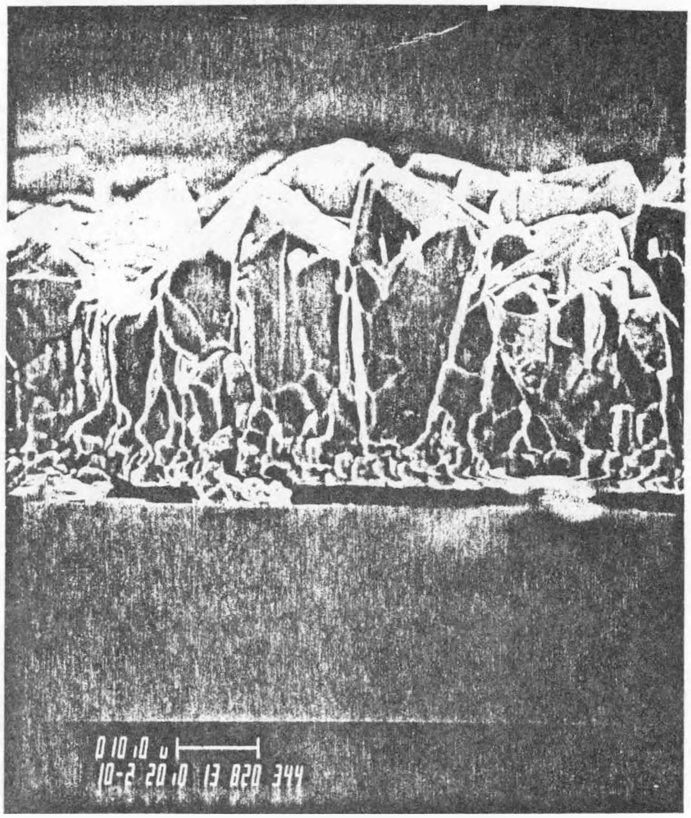

Fig. 6 Vertical cross section of a $CuInSe_2$ film on an alumina substrate showing the columnar growth of $CuInSe_2$.

X-ray diffraction technique using CuK$_\alpha$ radiation. Polycrystalline $CuInSe_2$ powder of random orientations is known to show the following strong diffractions and relative intensities. Figure 7 shows the diffraction spectrum

h k ℓ	{112}	{204} and {220}	{116} and {312}
2θ	26.66	44.36	52.45
I/I_o	70	100	85

of a typical $CuInSe_2$ films deposited on a graphite substrate. All known strong diffraction peaks associated with $CuInSe_2$ are present, indicating that the deposited film consists of a single phase material. The higher intensity at $2\theta = 26.66°$ suggests that the deposited films shows a slight preferred{112}. orientation.

The electrical resistivity of $CuInSe_2$ films depends on the nature of the transport agent and the type of the substrate. In general, the use of hydrogen iodide as a transport agent yields films with higher and more uniform resistivities than the films deposited by using iodine as a transport agent. Also, the resistivity of $CuInSe_2$ films deposited on ceramic substrates is higher than that on graphite or coated graphite substrates. The resistivity of $CuInSe_2$ films on alumina substrates was measured directly by the four probe technique, and the lateral resistivity profile was also readily obtained. The resistivity of $CuInSe_2$ films may be reduced by heating the film in a hydrogen-selenium mixture containing about 0.03% selenium at 750°C, as shown in Fig. 8. At lower temperatures, 600°C for example, the resistivity of $CuInSe_2$ films was not affected by selenium treatment. In general, films deposited at higher temperatures showed higher resistivity; however, there is no correlation between substrate

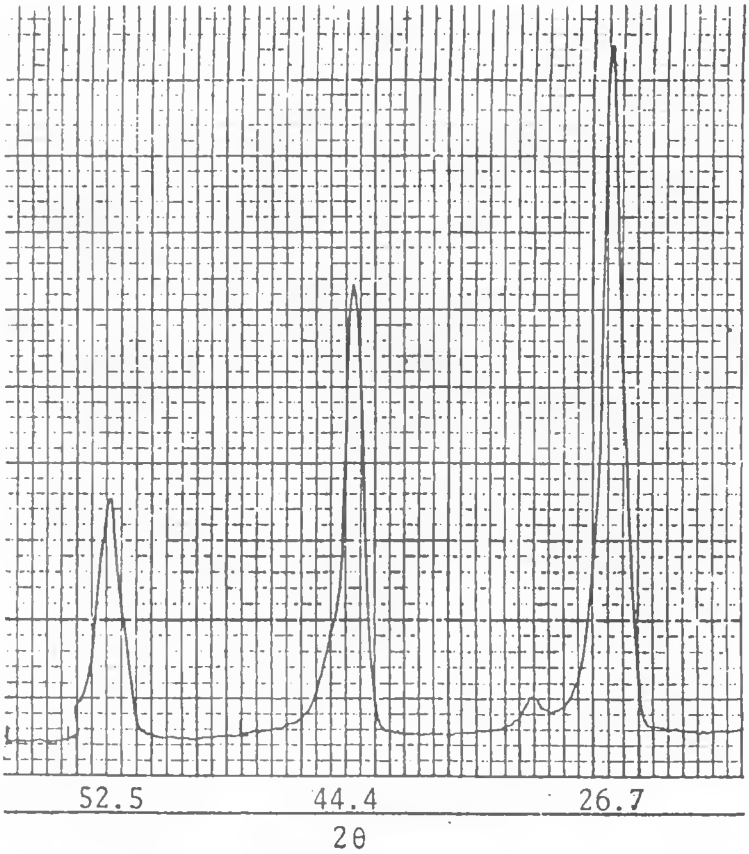

Fig. 7 X-ray diffraction spectrum of a CuInSe$_2$ film deposited on a graphite substrate by the CSCVT technique

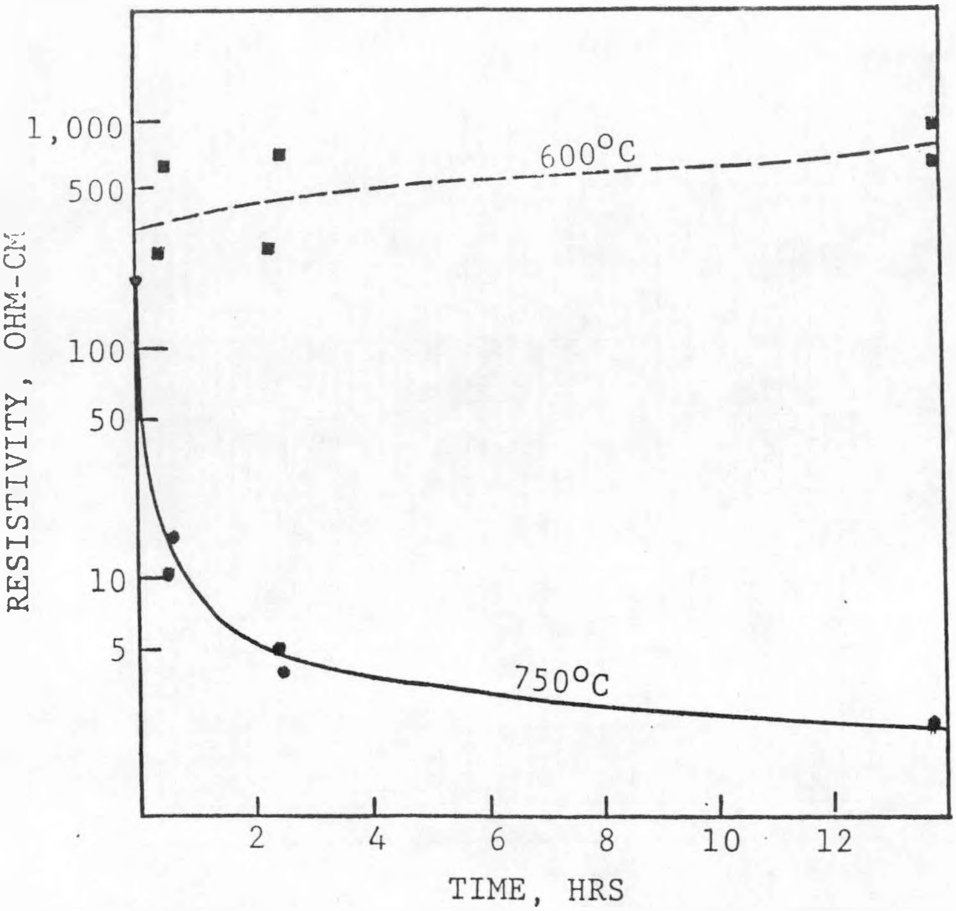

Fig. 8 Effect of selenium treatment at high temperatures on the resistivity of $CuInSe_2$ films on alumina substrates.

temperature and electrical resistivity in several sets of specimens. Further, there are considerable variations in resistivity in films deposited by using iodine as a transport agent; the resistivity inhomogeneity is more pronounced in films of high resistivities, and a factor 10 difference in various regions of the film is not uncommon. Associated with the resistivity inhomogeneity, variations in photoresponse have also been observed. By depositing zinc oxide films and gold films (ohmic contact) on the surface of $CuInSe_2$ films, variations in open-circuit voltage under simulated AM1 conditions were observed, and these variations appear to be related to resistivity inhomogeneities, i.e., higher V_{oc} in regions of higher resistivity. The resistivity of $CuInSe_2$ films deposited by using hydrogen iodide as a transport agent is usually uniform within a factor of two.

The measurement of electrical resistivity of $CuInSe_2$ films on conducting substrates requires the formation of ohmic contacts on the surface of $CuInSe_2$. Evaporated gold forms on ohmic contact with $CuInSe_2$ in most cases while the use of silver films requires heat treatment at 300°C. By passing current through the thickness direction of the specimen, the potential drops between different regions of the specimen may be measured to yield the ohmic contact/$CuInSe_2$ interface resistance and the sum of $CuInSe_2$ resistance and the $CuInSe_2$/substrate interface resistance. In a Ag/$CuInSe_2$/SiC-coated graphite structure, for example, the major portion of the potential drop occurs at the Ag/$CuInSe_2$ interface, and this contact resistance is usually on the order of 0.06-0.2 ohm-cm^2. The sum of the $CuInSe_2$ resistance and $CuInSe_2$/substrate interface resistance is 0.012-0.020 ohm-cm^2. Assuming that the $CuInSe_2$/substrate interface is negligible, the resistivity of $CuInSe_2$ (film thickness: 15 μm) is then 8-14 ohm-cm. In most

$CuInSe_2$ films on coated graphite substrates, the resistivity of the film is in the range of 5-20 ohm-cm, considerably lower than the resistivity of $CuInSe_2$ films deposited on alumina substrates. The reason for this low resistivity is not clear.

II.4 Heterojunction Solar Cells

Since the $CuInSe_2$ films deposited on alumina substrates are usually of considerable higher resistivity than those on coated graphite substrates, attempts were made to deposit an ohmic contact on the surface of alumina prior to the deposition of $CuInSe_2$ films. Gold films of about 2000 Å were evaporated onto the surface of alumina; however, gold was found to diffuse rapidly through the $CuInSe_2$ films at substrate temperatures higher than 550°C. The successive deposition of tungsten and carbon films on alumina was found to provide a conducting film with a sheet resistance of about 0.05 ohms per square (this sheet resistance is too high for efficient devices). $CuInSe_2$ films were then deposited on C/W/alumina substrates by CSCVT.

The most commonly used heterojunction partner for $CuInSe_2$ films is CdS or $Cd_xZn_{1-x}S$ deposited by vacuum evaporation. However, our evaporator for CdS films has not functioned properly to yield films with satisfactory properties. As a preliminary evaluation of the photovoltaic characteristics of $CuInSe_2$ films, zinc oxiode and cadmium oxide films deposited by the ion-beam sputtering technique were used as the heterojunction partner for convenience. Many heterojunction solar cells of 0.1 cm^2 area were made. Under simulated AM1 conditions, the open-circuit voltage is 150-250 mV, the short-circuit current density is 10-25 mA/cm^2, and the fill factor is 0.35-0.45. The low I_{sc} and F.F. are due to the high series resistance of the device. The best cell so far has an open-circuit voltage of 260 mV, a short-circuit current density of 25 mA/cm^2, and a fill factor of 38%, corresponding to a conversion efficiency of about 2.5%. This low conversion efficiency is believed, at least in part, to the damage of $CuInSe_2$ films by the ion-beam bombardment. Further work will be carried out using the vacuum evaporation or spraying technique for the deposition of the window layer.

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