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THIN FILM CADMIUM TELLURIDE SOLAR CELLS

Technical Progress Report No. 2, October 1—December 31, 1979

By
Ting L. Chu

January 1980

Work Performed Under Contract No. AC04-79ET23009

Southern Methodist University
Dallas, Texas

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Solar Energy

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Ting L. Chu, Principal Investigator
Southern Methodist University
Dallas, Texas 75275

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Summary

This is the Second Technical Progress Report of a research program "Thin Films Cadmium Telluride Solar Cells" supported by the U. S. Department of Energy under Contract No. DE-AC04-79ET23009. The objectives of this contract are to investigate thin films of cadmium telluride on low cost substrates and to demonstrate the feasibility of producing thin film cells with a conversion efficiency of 10% or higher.

During this reporting period, the chemical vapor deposition of cadmium telluride films on foreign substrates by the direct combination of the elements has been further investigated. Inert substrates such as graphite and tungsten/graphite are not suitable for the deposition of device quality cadmium telluride films because of the rectifying interface and pinhole problems. Indium coated W/graphite form an ohmic contact with n-type cadmium telluride, and the deposited films are essentially free of pinholes. The properties of Ag/n-CdTe/In/W/graphite structures, such as the current-voltage characteristics as a function of temperature, the barrier height, the photovoltaic properties, and the intragrain diffusion length in cadmium telluride, have been investigated. Preliminary work has also been carried out on the deposition of p-type cadmium telluride films on Sb/W/graphite substrates.

The reaction between cadmium iodide and tellurium in a hydrogen atmosphere has been concluded to be unsuitable for the deposition of cadmium telluride films.

I. Introduction

This is the Second Technical Progress Report of a research program "Thin Films Cadmium Telluride Solar Cells" supported by the Department of Energy under Contract No. DE-AC04-79ET23009. The objectives of this contract are (1) to conduct research and development of thin film cadmium telluride solar cells on low-cost substrates, and (2) to demonstrate the feasibility of producing thin film cells with a conversion efficiency of 10% or higher.

The technical approaches used in this program consist of (1) the chemical vapor deposition of cadmium telluride films of controlled conductivity type and carrier concentration on a suitable foreign substrate with low CdTe/substrate interface resistance, (2) the characterization of structural and electrical properties of the deposited films, and (3) the fabrication, evaluation, and optimization of thin film cadmium telluride solar cells.

Graphite is an economical substrate for large area solar cells. Several types of graphite, such as grade PLC graphite manufactured by POCO Graphite Incorporated and grade CC-49 graphite manufactured by Stackpole Carbon Company, have a thermal expansion coefficient similar to that of cadmium telluride, $5.5 \times 10^{-6}\,^{o}C^{-1}$. However, low-cost graphite is porous, and its surface is inhomogeneous. A thin layer of aluminum, carbon, indium, silicon, or tungsten has been deposited on graphite to provide a more impervious and uniform surface. With the exception of In/Graphite, cadmium telluride films deposited on coated graphite substrates by the reaction of cadmium and tellurium in a hydrogen flow has been found to form a rectifying interface with the substrate. The use of the indium layer has also reduced considerably the pinhole density in cadmium telluride films.[1]

During the past quarter, the deposition and characterization of cadmium telluride films on foreign substrates, including W/Graphite, Al/W/Graphite, In/W/Graphite, and Sb/W/Graphite, have been studied in more detail with the objective of producing low resistance ohmic contacts to both n- and p-type cadmium telluride. The deposition apparatus has been modified to deposit indium in-situ on W/Graphite substrates just prior to the deposition of cadmium telluride films by the direct combination of the elements. Schottky barriers formed on CdTe/In/W/Graphite structures have been used to evaluate the electrical and photovoltaic properties of cadmium telluride films. In addition to the direct recombination of the elements, the reaction between cadmium iodide and tellurium in a hydrogen atmosphere has been investigated for the deposition of cadmium telluride films. The experimental procedures and results are discussed in the following sections.

II. Technical Discussion

Two types of reactions have been selected for the deposition of cadmium telluride films:

(1) Reactions between elemental cadmium and tellurium

$$2\ Cd(g) + Te_2(g) \rightarrow 2\ Cd\ Te\ (s)$$

(2) Reactions between cadmium iodide and tellurium in a hydrogen atmosphere

$$2\ H_2(g) + 2\ Cd\ I_2(g) + Te_2(g) \rightleftarrows 2\ Cd\ Te(s) + 4\ HI\ (g)$$

Reaction (1) is the most economical process for the deposition of cadmium telluride films and has the flexibility that the Cd/Te molar ratio in the reactant mixture can be readily varied. Reaction (2) is chemically reversible, and this reversibility could improve the microstructure of deposited films. Both reactions have been used for the deposition of cadmium tellurium films. However, major efforts have been directed to the deposition and characterization of cadmium telluride films on several foreign substrates by the direct combination of the elements.

II. 1. Cadmium Telluride Films on Inert Substrates

The deposition of cadmium telluride films on W/Graphite and other inert substrates by the reaction of cadmium and tellurium has been studied in more detail. It is desirable that a continuous pinhole-free film is formed at small thicknesses.

The mechanism of vapor deposition process is fairly well understood. The initial stage involves the formation of isolated nuclei which act as growth centers. The enlargement of crystallites around the nuclei and the subsequent coalescence of all adjacent crystallites complete the film deposition process. The thickness at which the film becomes continuous is related to the density of initial nuclei and the ratio of growth rates in the thickness and lateral directions of the crystallites. A high density of initial nuclei is essential since further deposition takes place preferentially on these nuclei rather than on the surface of a foreign substrate. The density of initial nuclei is related to the substrate surface topography, the substrate-deposit interaction, the substrate temperature, and the reactant composition. The substrate temperature is most important. At low temperatures, initial nucleation takes place readily providing a high density of nuclei, and the film becomes continuous at relatively small thicknesses. However, the average size of crystallites is also small.

The initial stage of deposition of cadmium telluride on a tungsten/graphite substrate at 500°C is shown at two magnifications in Fig. 1, where the nominal thickness of the film is about 2 μm. The crystallites are of random shape and size, up to about 5 μm, and pinholes are present in many areas. Further deposition of cadmium telluride to a thickness of 20 - 30 μm cannot completely eliminate the pinholes; an example is shown in Fig. 2. The presence of pinholes in these films is due mainly to the facts that after the initial nuclei are formed, cadmium telluride tends to deposit preferentially on these nuclei to form irregularly shaped crystallites and that the coalescence of adjacent crystallites cannot grow over all pinholes. Although pinhole-free small area devices, a few mm^2, can be made from these films, attempts to make large area, 1 cm^2 for example, devices have not been successful.

The nucleation and growth of cadmium telluride films on other inert substrates, such as mullite and carbon/graphite, are very similar to those

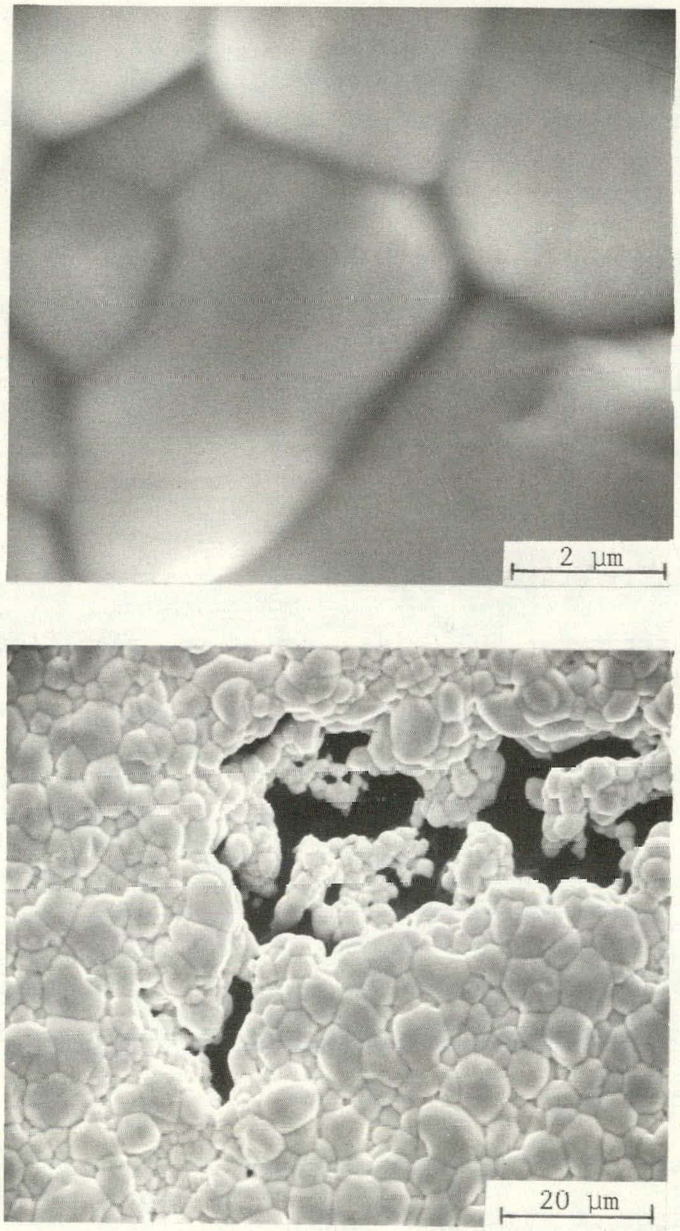

Figure 1 The initial stage of deposition of cadmium telluride, about 2 µm thickness, on a tungsten/graphite substrate at 500^{o}C.

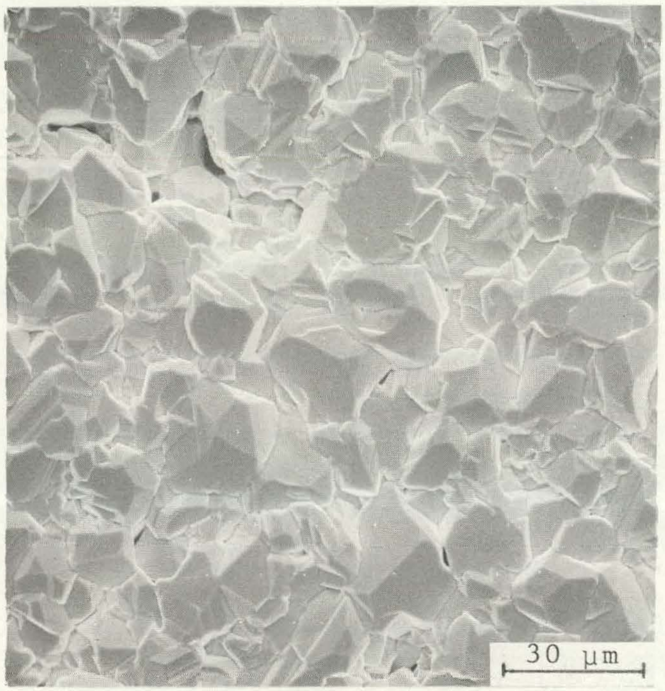

Figure 2 As-deposited surface of a cadmium telluride film of about 20 μm thickness on a tungsten/graphite substrate showing pinholes in the film.

on tungsten/graphite substrates. Large area pinhole-free films have not been produced. Further, cadmium telluride films formed by the direct combination of elements have low carrier concentrations, less than 10^{13} cm^{-3}. Small area Schottky barriers formed on CdTe/C/Graphite and CdTe/W/Graphite structures all show rectifying interfaces as shown by current-voltage measurements. It is therefore concluded that inert substrates such as carbon or tungsten coated graphite are not suitable for the deposition of device quality cadmium telluride films.

II. 2. Cadmium Telluride Films on Reactive Substrates

For device purposes, the substrate must form a low resistance ohmic contact with the cadmium telluride film. In principle, the contact material for n-type cadmium telluride should have a work function smaller than that of cadmium telluride, and for p-type cadmium telluride, the contact material should have a larger worker function. Under these conditions, a barrierless contact to cadmium telluride is obtained. When a barrierless contact cannot be obtained by a suitable choice of contact material, the contact resistance may be reduced by lowering the barrier height or decreasing its thickness. The tunneling current through a barrier is proportional to $\exp(-C\phi^{\frac{1}{2}}t)$, where ϕ is the barrier height and t its thickness (t is proportional to $N^{-\frac{1}{2}}$, where N is the net carrier concentration). Hence a very substantial increase in tunneling current may be obtained by creating a region of high carrier concentration under the contact either through alloy regrowth or in-diffusion of a suitable dopant provided by the contact material.

The electron affinity of cadmium telluride is 4.3 eV. The work function of n^{+}-CdTe is similar to the electron affinity, while that of lightly doped n-CdTe is several tenths of an eV higher than the electron affinity. The work function of group III metals, aluminum, gallium, indium, and thallium, is in the range of 3.6 - 4.2 eV. Since this is the right relation for barrierless contacts, all group III metals should form good ohmic contacts to n-type cadmium telluride. Since the work function of p-type cadmium telluride is higher than 5 eV, common metals are not suitable as ohmic contacts. The alloying technique may be used to produce a heavily doped region at the p-CdTe/substrate interface.

Both Al/W/Graphite and In/W/Graphite substrates have been used for the deposition of cadmium telluride films by the direct combination of the elements. Aluminum and indium films of about 1 μm thickness were deposited on W/Graphite substrates by evaporation. The deposition of cadmium telluride films was carried out in the temperature range 500° - 600°C. When Al/W/Graphite was used as the substrate, the specimen was heated at 675°C (m.p. of Al: 660.2°C) for 10 min after initial deposition so that molten aluminum will form an intimate contact with cadmium telluride. Subsequently, the substrate temperature was reduced and the deposition completed. The current-voltage measurements of Schottky barriers prepared from many n-CdTe/Al/W/Graphite structures indicate that the CdTe/Al interface is rectifying, due presumably to the presence of oxide on the substrate surface. On the other hand, Schottky barrier characteristics of Ag/n-CdTe/In/W/Graphite structures indicate that n-CdTe/In interface is ohmic. Their properties will be discussed in detail in the next section.

Sb/W/Graphite substrates prepared by the evaporation of antimony onto W/Graphite has also been used for the deposition of cadmium telluride films by the direct recombination of elements using phosphine as a dopant. After the initial deposition at 500°C, the specimen was heated at 650°C (m.p. of Sb: 630.5°C) for 10 min to insure the reaction between antimony and cadmium telluride, and the subsequent deposition was completed at $500 - 550^\circ$ C. The concentration of phosphine in the reactant mixture was varied over a wide range with a P/Cd molar ratio of up to 0.1. It is assumed that the reaction of cadmium telluride with molten antimony will yield a heavily doped p-region at the interface. About fifteen experiments have been carried out, and Schottky barriers prepared from these films exhibit high resistance in both directions of current flow. However, most of these films have been found to be n-type from photovoltage measurements, and no conclusions on the CdTe/Sb interface resistance can be deduced. Further investigations will be carried out.

II. 3. Cadmium Telluride Films on In/W/Graphite Substrates

Since the use of an indium interlayer provides an ohmic contact to n-type cadmium telluride, the deposition apparatus has been modified so that indium can be deposited on the substrate surface in situ just prior to the deposition of cadmium telluride films. The modified apparatus is shown schematically in Fig. 3, where an indium container is maintained at a higher temperature than the substrate. Hydrogen chloride is used to convert indium into indium monochloride which disproportionates on the substrate surface to deposit indium. The chemical reactions are:

$$2\ \mathrm{In}\ (\ell) + \mathrm{HCl}\ (g) \rightarrow 2\ \mathrm{InCl}\ (g) + \mathrm{H_2}\ (g)$$

$$3\ \mathrm{InCl}\ (g) \rightarrow 2\ \mathrm{In}\ (\ell) + \mathrm{InCl_3}\ (g)$$

In addition to reducing the CdTe/substrate interface resistance, the use of an indium interlayer, a liquid at temperatures used for the deposition process, also facilitates the nucleation of cadmium telluride. Large area pinhole-free cadmium telluride films can be routinely produced. Figure 4 shows the as-deposited and fractured cross-section surfaces of a cadmium telluride film of about 30 μm thickness on an In/W/Graphite substrate. The deposited film is essentially polycrystalline with no

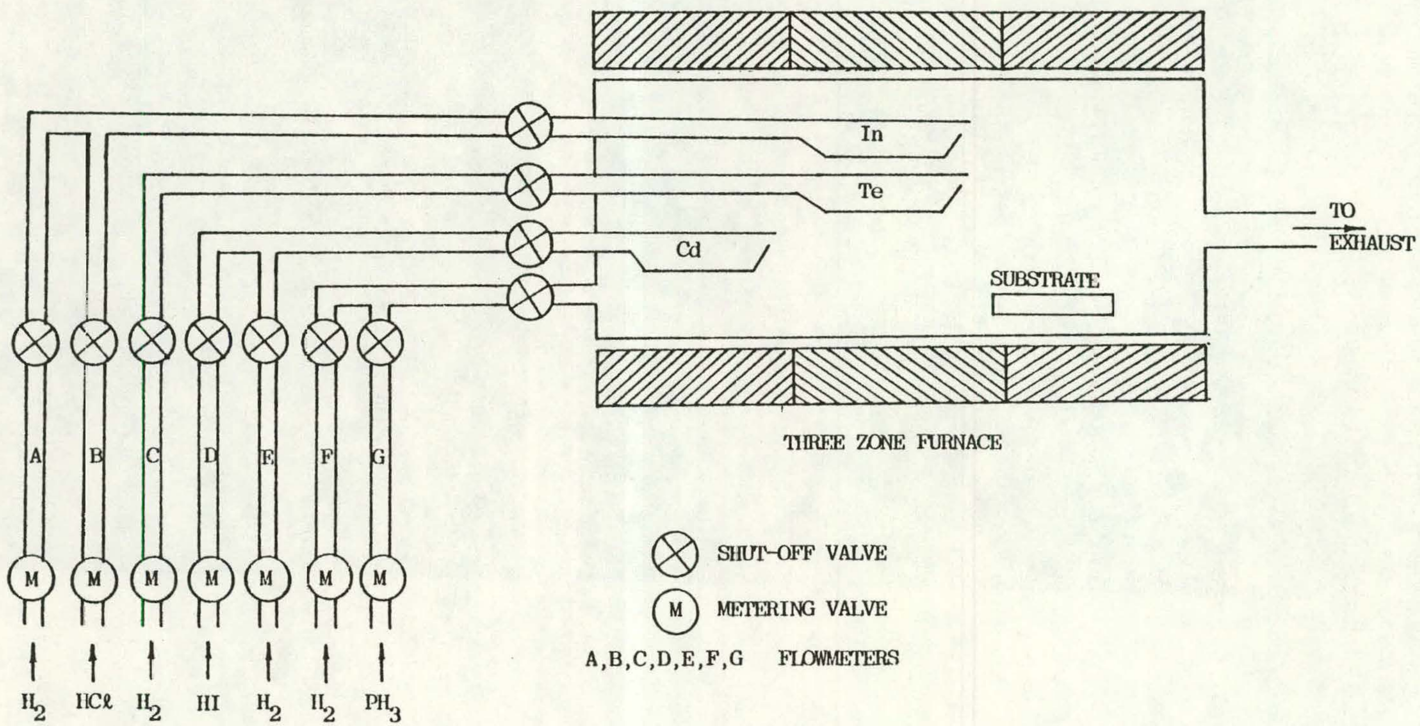

Figure 3 Schematic diagram of the modified apparatus for the deposition of cadmium telluride films.

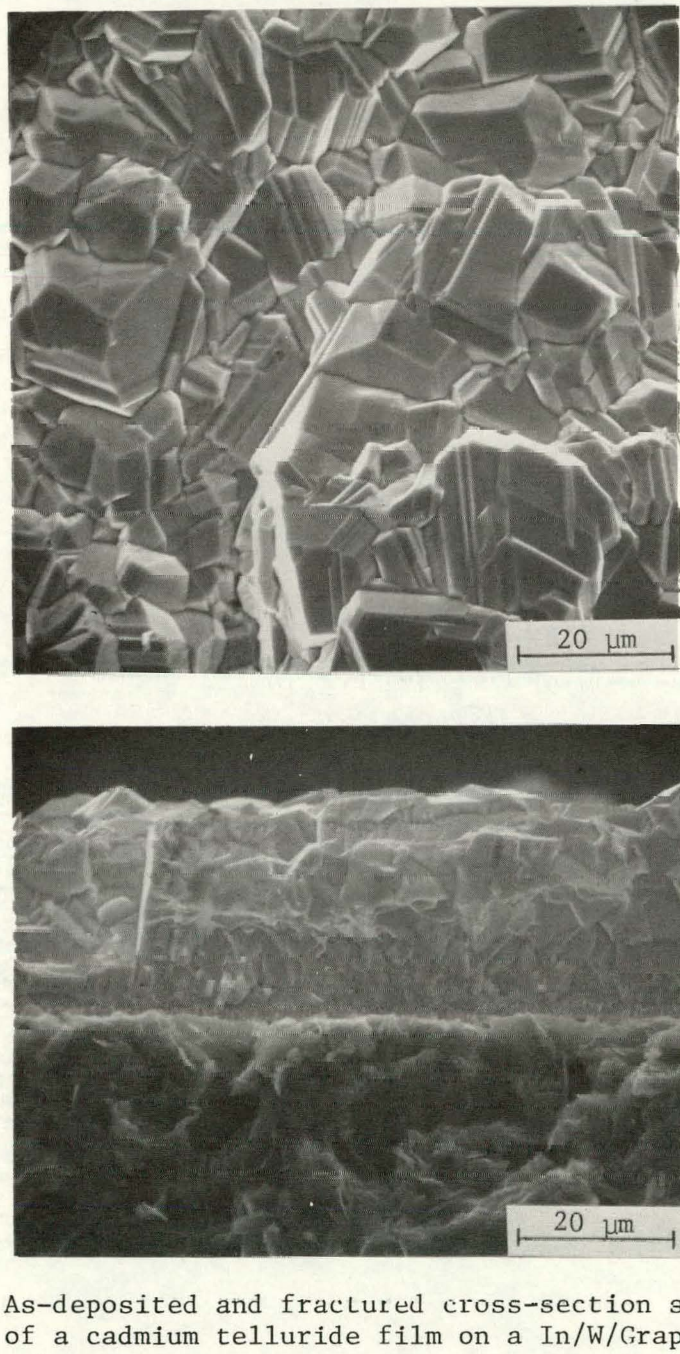

Figure 4 As-deposited and fractured cross-section surfaces of a cadmium telluride film on a In/W/Graphite substrate.

appreciable preferred orientations, as shown by X-ray diffraction.

When hydrogen iodide was used as a dopant during the deposition of cadmium telluride films, the carrier concentration in the film has been calculated to be (1-3) x 10^{13} cm^{-3} from differential capacitance measurements. This carrier concentration is similar to that in cadmium telluride films deposited on mullite substrate under similar conditions. Assuming that the carrier mobility in cadmium telluride films on In/W/Graphite substrate is similar to that on mullite substrate, 20 - 30 cm^2/V-sec, deduced from the Hall measurements, the resistivity of cadmium telluride film is thus (3-8) x 10^3 ohm-cm. The carrier concentration in cadmium telluride films cannot be further increased by increasing the flow rate of hydrogen iodide in the reactant mixture. Also, cadmium telluride is etched when the concentration of hydrogen iodide in the reactant mixture exceeds about 0.5% by volume.

Schottky barriers have been prepared from many cadmium telluride films deposited on In/W/Graphite substrates by evaporating silver dots of 0.5 - 2 mm^2 area onto the surface of the specimen. Their current-voltage characteristics were measured by mounting the specimen in a brass chamber, and glass-metal feedthroughs were used to provide current and voltage connections from the diodes to the measurement equipment. The entire chamber was placed in a constant temperature bath containing silicone oil. The measurements were carried out by the four-probe technique in the temperature range of 25° to 90° C. Figure 5 shows the current-voltage characteristics of one Schottky barrier at 476°, 58.2°, 74.8°, and 90.2° C. At low voltages, the ℓn I versus V relation in the forward direction is linear, and at these temperatures, the diode quality factor "n" is about 1.5, 1.7, 1.9, and 2.1, respectively. The larger "n" values at higher temperatures are presumably related to the more pronounced contribution

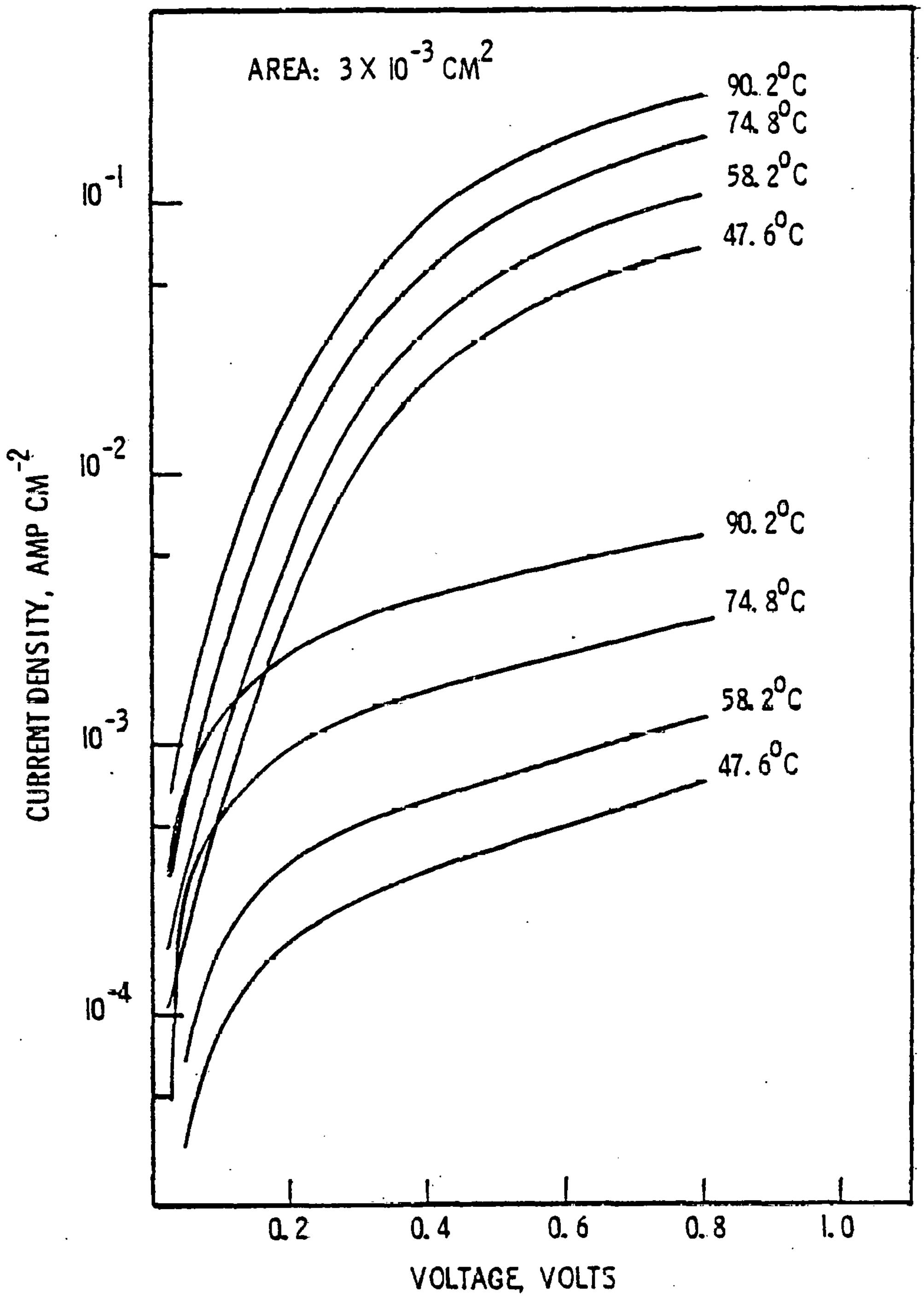

Figure 5 Dark current voltage characteristics of a Ag/CdTe/In/W/Graphite structure as a function of temperature.

of the series resistance of the device. The series resistance dominates the current flow at voltages higher than about 0.3 V. The reverse current also increases with increasing temperature as expected. The plot of the logarithm of reverse current at 0.5 V versus reciprocal temperature yields a straight line with an activation energy of about 0.57 eV. The significance of this activation energy is not clear at present.

The barrier height in Ag/CdTe(I-doped)/In/W/Graphite structures was measured by the photoresponse method. The apparatus consists of a source of monochromatic light, a light detector with known spectral response, and a lock-in amplifier for measuring the output of the device. An example of the photoresponse data is shown in Fig. 6, where the square root of photoresponse versus photon energy relation is linear. The barrier height in this device obtained from the least square fit is 0.76 eV.

Schottky barrier structures of the configuration Ag/CdTe/In/W/Graphite have also been used for the measurements of effective intragrain diffusion length in cadmium telluride films by the scanned electron beam method. Large grain specimens with flat surfaces are selected, and a Schottky barrier is formed to cover only a small portion of the grain under investigation. An ETEC Autoscan SEM was used to provide simultaneous measurement of beam position and current response as the electron beam was moved away from the edge of the Schottky barrier. The experimental arrangement is shown schematically in Figure 7. The electron beam was accelerated by 20 kV, and the penetration depth is of the order of 2.5 μm. Thus, the carrier generations volume has a pencil-like shape with a length of about 0.45 μm and a width of about 0.08 μm.[2] Since the grains under

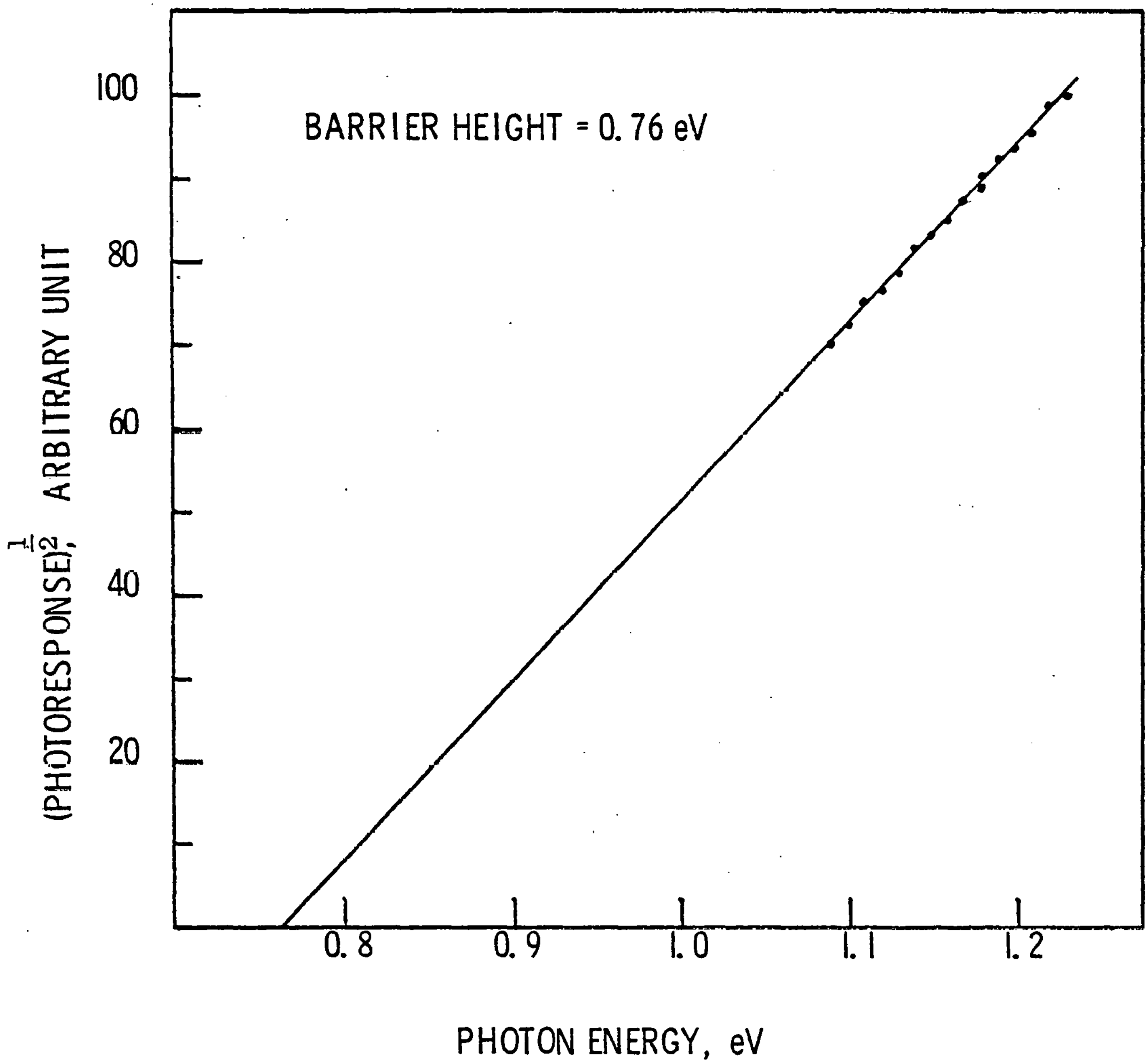

Figure 6 The photoresponse of a Ag/CdTe/In/W/Graphite structure as a function of photon energy.

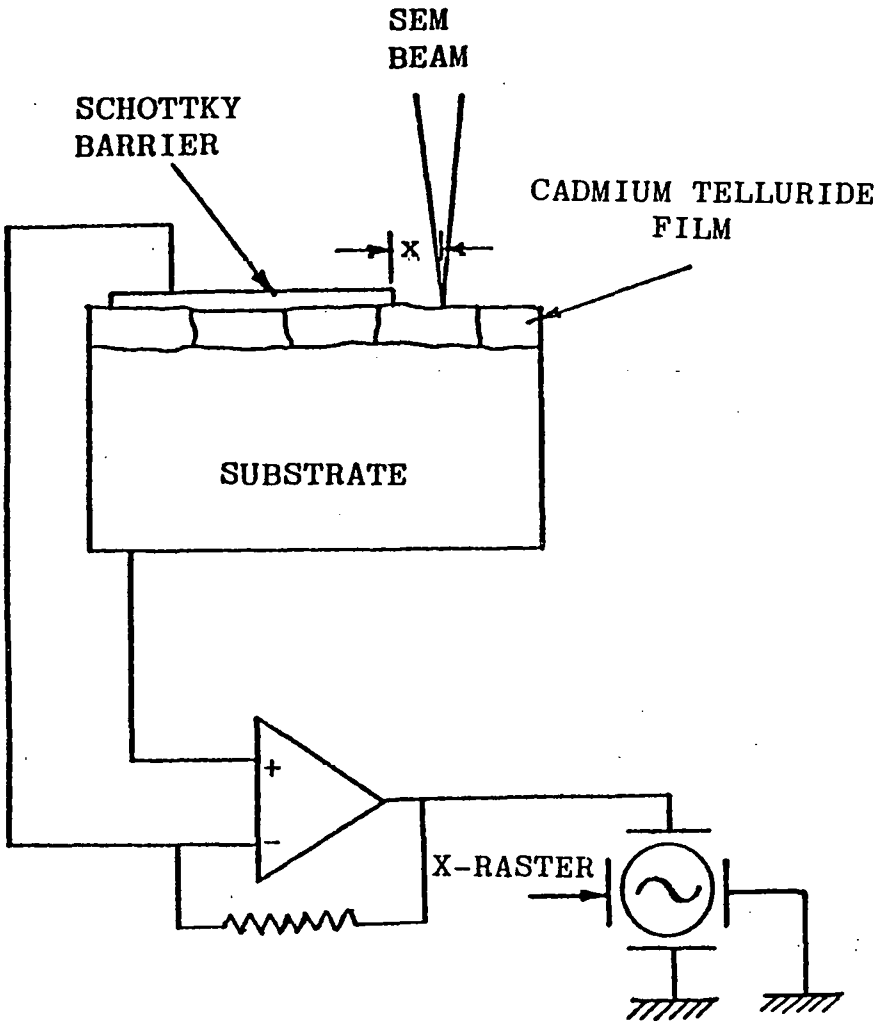

Figure 7 Schematic diagram of the apparatus for the determination of intragrain diffusion length in cadmium telluride films.

investigation have a smallest dimension of 10 μm or larger, the scanned electron beam technique is valid for the measurement of effective intragrain diffusion length. Figure 8 shows examples of an induced current versus position photograph and the digitized data obtained with a HP 6825 calculator and 7225 A X-Y plotter-digitizer, where the effective intragrain diffusion length is of the order of 1 μm. The intragrain diffusion length measured for a number of undoped and iodine-doped cadmium telluride films is in the range of 0.8 - 1.8 μm.

Several Schottky barrier solar cells of 1 cm^2 area have been prepared in the following manner. A gold or silver film of 60 - 80 Å thickness was evaporated onto the surface of cadmium telluride films deposited on In/W/Graphite substrates under a pressure of less than 10^{-6} Torr. The grid contact, 10 lines per cm, was formed by the evaporation of silver through a metal mask. The current-voltage characteristics of the solar cells were measured under illumination with G. E. ELH quartz-halogen lamps equivalent to AM1 conditions. The short-circuit current density is usually 10 - 12 mA/cm^2; however, the low open-circuit voltage, about 300 mV, and low fill factor, 36 - 39%, result in poor conversion efficiencies. The low open-circuit voltage is due mainly to the excessive dark current through the barrier. The high dark current is believed to be associated with grain boundaries in the films; grains in the vapor deposited cadmium telluride are not as tightly packed as in melt-grown material, and metals could penetrate into grain boundaries during contact formation resulting in high shunting current. The low fill factor is due to the high series resistance of the device structures. Attempts to determine the individual contributions of the CdTe/substrate interface and the cadmium telluride film to the series resistance were not successful.

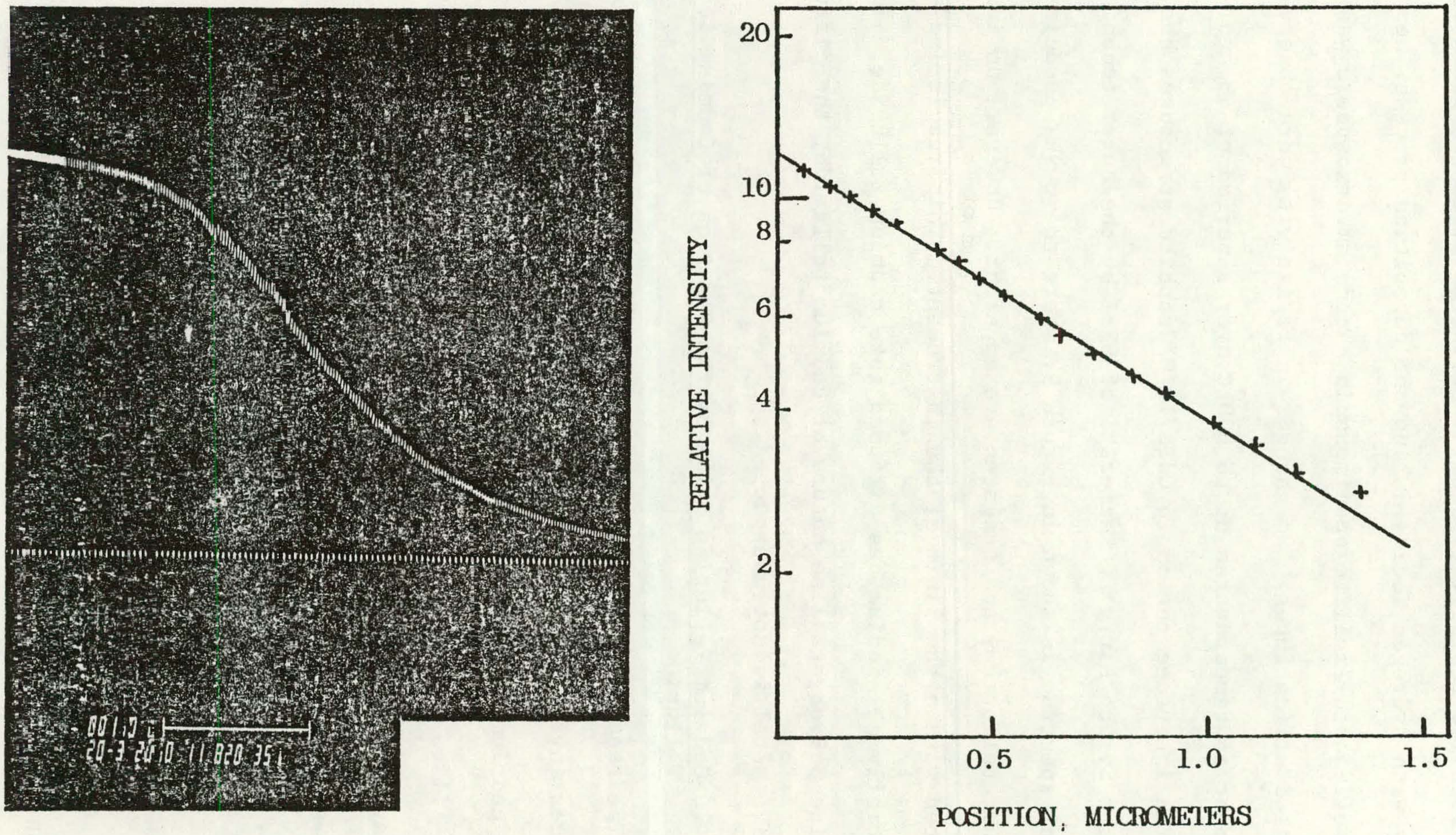

Figure 8 The beam induced current versus position photograph and the digitized data for the determination of effective intragrain diffusion length in a cadmium telluride film.

Since low resistivity cadmium telluride films cannot be obtained by doping with hydrogen iodide during the deposition process, heat treatment of CdTe(I-doped)/mullite specimens in a cadmium atmosphere was carried out in sealed silica tubes. No changes in resistivity were observed after heat treatment at temperatures up to 600°C over a period of 48 hrs.

The interface region in CdTe/In/W/Graphite structures has been examined by Dr. Larry L. Kazmerski of SERI by the Auger technique. A typical spectrum is shown in Figure 9, where the peaks associated with cadmium, tellurium, and tungsten are apparent. However, no indium can be detected within the limit of the instrument. This result indicates that essentially all indium has diffused into cadmium telluride. In view of the fine polycrystalline nature of cadmium telluride, the diffusion of a reactive metal is not unexpected.

II. 4. Cadmium Telluride Films by the Reaction of Cadmium Iodide and Tellurium

The reaction of cadmium iodide and tellurium in a hydrogen atmosphere has been investigated for the deposition of cadmium telluride films. C.P. grade cadmium iodide, purchased from Baker Chemicals Co., was placed in a fused silica container, which replaced the cadmium container in the deposition apparatus. Since cadmium iodide has a lower vapor pressure than cadmium, the cadmium iodide container must be maintained at a higher temperature, 600°C. When hydrogen is used as a carrier gas to vaporize cadmium iodide, cadmium iodide is partially reduced to cadmium, liberating hydrogen iodide. Thus, the reactant mixture consists of a mixture of cadmium, tellurium, cadmium iodide, hydrogen, and hydrogen iodide. Because of the high concentration of hydrogen iodide in the reactant mixture, no continuous films could be obtained.

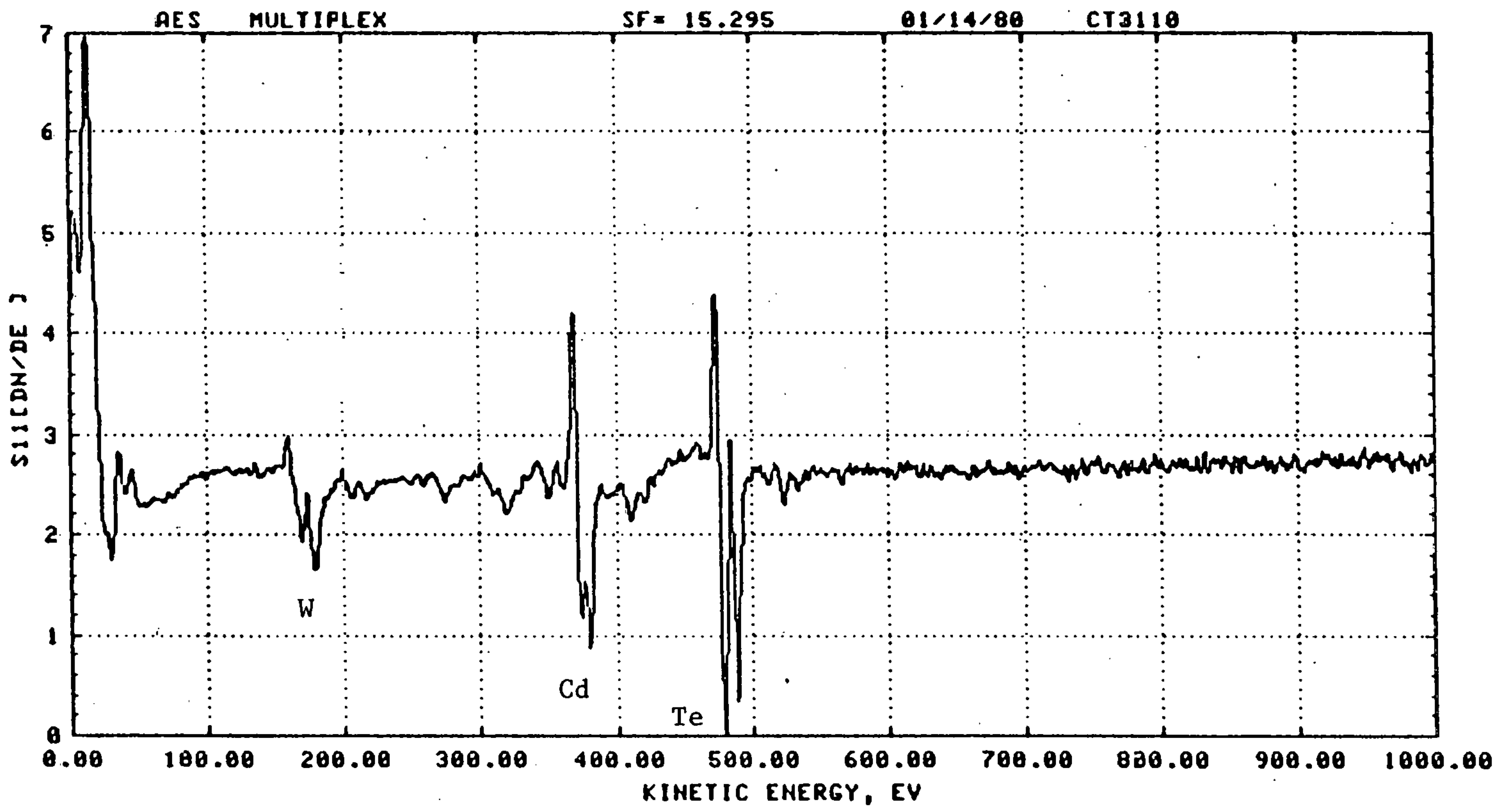

Figure 9 Auger spectrum of a CdTe/In/W/Graphite structure at the CdTe/substrate interface region.

III. Conclusions

1. Inert substrates such as graphite and W/graphite are not suitable for the chemical vapor deposition of device quality cadmium telluride films.

2. Indium coated W/Graphite forms an ohmic contact with cadmium telluride and is suitable for the deposition of pinhole-free films. However, the use of hydrogen iodide as a dopant during the deposition process yields only high resistivity material, and heat treatment in a cadmium atmosphere at temperatures up to $600^{o}C$ has not produced any appreciable changes.

3. Grain boundaries in, and high resistivity of, cadmium telluride limit the photovoltaic performance of Ag/n-CdTe/In/W/Graphite structures.

4. The reaction between cadmium iodide and tellurium in a hydrogen atmosphere is unsuitable for the deposition of continuous cadmium telluride films.

IV. References

(1) "Thin Film Cadmium Telluride Solar Cells," Technical Progress Report No. 1, DOE Contract DE-AC04-79ET23009, October, 1979.

(2) T. E. Everhart and P. H. Hoff, "Determination of Kilovolt Electron Energy Dissipation vs Penetration Distance in Solid Materials," J. Appl. Phys., 42, 4837(1971).

V. Plan for the Next Period

1. Heat treatment of doped cadmium telluride films in a controlled atmosphere in sealed tubes.

2. The use of thallium coated graphite substrate for the deposition of n-type cadmium telluride films.

3. The deposition of cadmium sulfide on graphite substrates and the use of CdS/Graphite as a substrate for the deposition of n-type cadmium telluride films.

4. The deposition of p-type cadmium telluride films by using arsine as a dopant.

5. Further investigations on the use of Sb/W/Graphite as substrates for the deposition of p-type cadmium telluride films.

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