MASTER

THIN FILM CADMIUM TELLURIDE SOLAR CELLS

FINAL TECHNICAL REPORT

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by

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Summary

This is the Final Technical 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 determine the feasibility of using these films for high efficiency solar cells.

Efforts during this program have been directed to the construction of apparatus for the chemical vapor deposition of cadmium telluride films, the selection and preparation of substrates, the deposition and characterization of cadmium telluride films, and the fabrication and characterization of solar cells. Cadmium telluride films have been deposited on a number of substrates by the direct combination of cadmium and tellurium on the substrate surface at 500°C or higher at rates of up to 0.6 μm/min. The structural, crystallographic, and electrical properties of cadmium telluride films deposited over a wide range of conditions have been evaluated. A series of doping experiments have been carried out using iodine and indium as the n-type dopant, and phosphorus, arsenic, and antimony as the p-type dopant. Low resistivity films have not been produced thus far. In/W/graphite substrates have been used for the deposition of n-type films with an ohmic interface. However, no suitable substrates have been found to form an ohmic interface with p-type films. Solar cells prepared from these films exhibit relatively good short-circuit current density, up to 15 mA/cm^2, but their conversion efficiencies are severely limited by the high series resistance of the devices.

It is believed that low resistivity cadmium telluride films can be prepared by optimizing the deposition conditions. In parallel with the search of substrates with low interface resistance, back wall cells, such as p-CdTe/n-CdS/ITO/glass(substrate), should be investigated.

I. Introduction

This is the Final Technical 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 determine the feasibility of using these films for high efficiency solar cells.

Cadmium telluride is a direct gap semiconductor with a room temperature band gap energy of 1.50 eV and is a promising thin film photovoltaic material. Its solar cells have a higher theoretical conversion efficiency than silicon and gallium arsenide cells.(1) Because of its sharp optical absorption edge and large absorption coefficients, solar radiation with energy in excess of the energy gap is essentially all absorbed within 2-3 μm of the surface, and a relatively short minority carrier diffusion length in the material can be tolerated. The present knowledge on the deposition of cadmium telluride films and the preparation of thin film solar cells are briefly reviewed below.

I. 1 Deposition of Cadmium Telluride Films

The preparation of cadmium telluride films requires a detailed knowledge of the pressure, temperature, and composition relations in the cadmium-tellurium system. The temperature-composition relation of the cadmium-tellurium system is well established and is reproduced in Figure 1.(2) It has a maxiumum melting point of 1092° ± 1°C at the stoichiometric composition, an eutectic temperature of 324° ± 2° on the cadmium-rich side, and an eutectic temperature of 449° ± 2°C on the tellurium-rich side

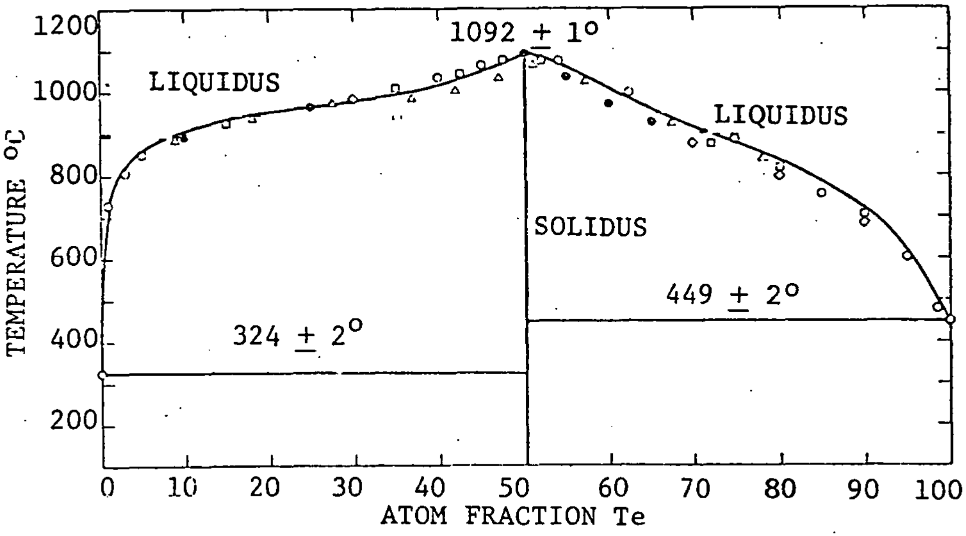


Figure 1 Temperature-composition relation for the cadmium-tellurium system.

(about 99% tellurium). The homogeneity region of cadmium telluride may be as high as 1% (atomic) on both the cadmium-rich and tellurium-rich sides of the stoichiometric composition.

At high temperatures, cadmium telluride dissociates into the elements according to the following equation (no CdTe molecules have been detected in the gas phase):

$$2\ \mathrm{CdTe(s)} \rightleftarrows 2\ \mathrm{Cd(g)} + \mathrm{Te_2(g)}$$

The partial pressure of cadmium is twice the partial pressure of tellurium, and the partial pressure of tellurium may be approximated by:

$$\log P_{\mathrm{Te_2}}\ (\mathrm{atm}) = 6.346 - (10000/T)$$

The dissociation pressure of cadmium telluride in the temperature range $500^o - 1000^oC$ is shown in Fig. 2, where the vapor pressures of elemental cadmium and tellurium are also shown for comparison. Thus, during the high temperature deposition and processing of cadmium telluride, an external pressure of cadmium or tellurium must be used to suppress the decomposition of cadmium telluride.

The deposition of cadmium telluride films have been carried out by vacuum evaporation, sublimation in an inert atmosphere, chemical transport, and electolytic techniques.

In the vacuum evaporation technique, cadmium telluride or the constituents may be used as the source material; the nature of the substrate, the substrate temperature, and deposition rate are the most important parameters affecting the properties of deposited films. The growth of films of cadmium chalcogenides on single crystalline foreign substrates, such as sodium chloride, potassium chloride, mica, germanium, silicon, etc. has been extensively reviewed; epitaxial films of both zincblende and wurtzite structures have been obtained at substrate temperatures up to 500°C.(3) When glass is used as a substrate, (4) stoichiometric crystalline films with zincblende structure has been obtained. To avoid condensation of free tellurium, substrate temperatures above 150°C are required, and the grain size depends strongly on substrate temperature. At 150°C, films about 0.5 μm thick have grain sizes of 1000-2500 Å with a preferred (111) orientation. Above 200°C, the accommodation coefficient of condensation decreases sharply. Regardless of deposition temperature, all films have resistivities of 10^7 ohm-cm or higher, even if dopants are added to the source material. The incorporation of impurities into cadmium telluride and the contribution

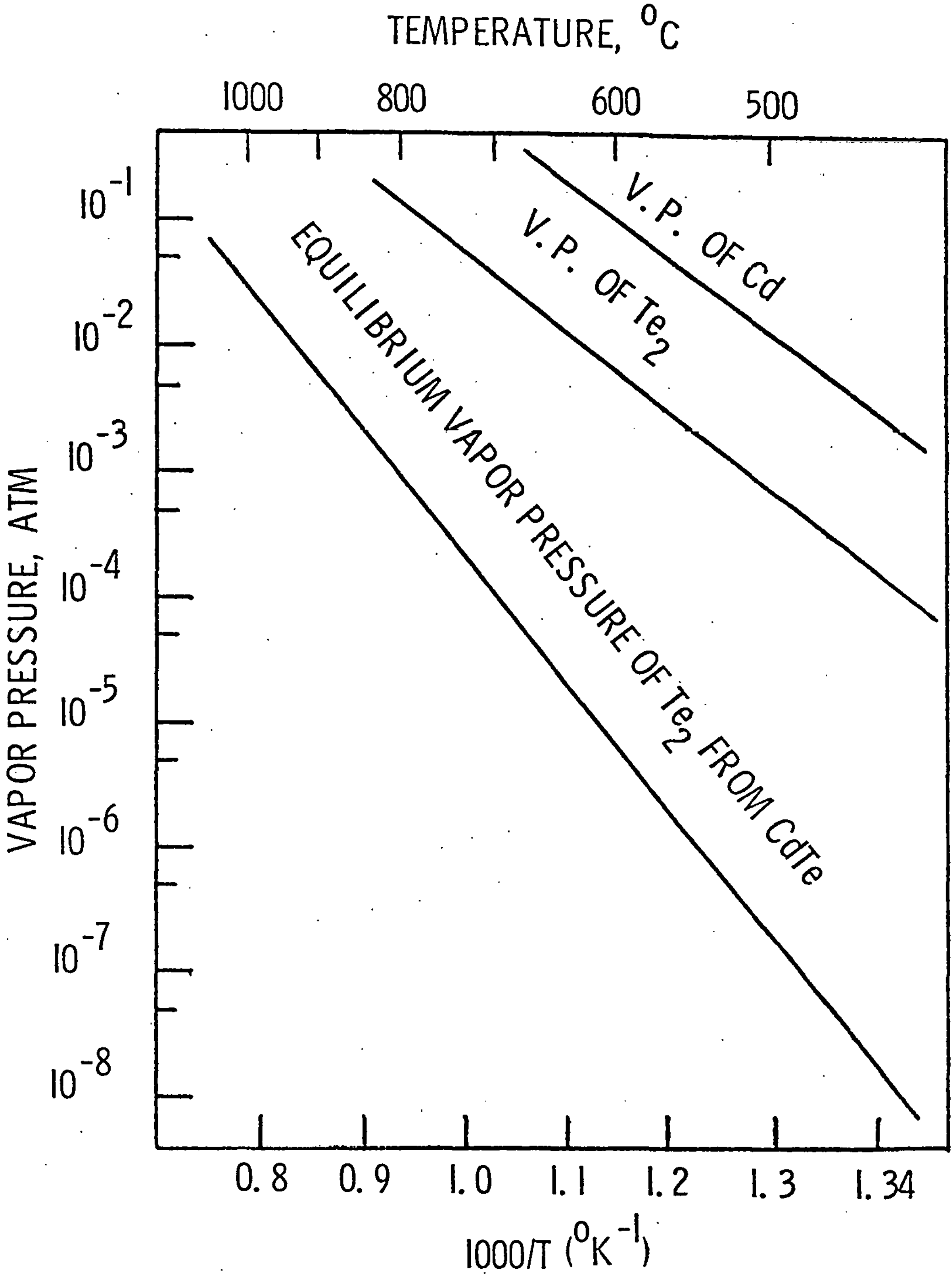


Fig. 2 The equilibrium vapor pressure of tellurium from the dissociation of cadmium telluride and the vapor pressures of elemental cadmium and tellurium in the temperature range 500°-1000°C.

of incorporated impurities to conductivity depend on the preparation conditions. In the single crystal growth process, indium is an effective donor only if the crystal has been annealed in cadmium vapor to establish a metal excess, and crystals containing copper or gold show p-type conductivity only if a tellurium excess has been formed.(5) If the cadmium telluride films deposited at or below 250°C do not show significant deviations from stoichiometry, neither acceptor nor donor impurities are electrically active. By heating films in evacuated quartz tubes together with small quantities of cadmium, gallium-indium, or tellurium at 500°-575°C for an hour, the dark resistivity has been reduced to about 10^3 ohm-cm. Films annealed in the presence of cadmium showed n-type conductivity while those heated in tellurium were p-type. Vacuum evaporation and sputtering have also been used by Entine, et al. and Vedam et al., respectively, under the DOE and SERI sponsored programs.(6,7)

The "hot wall epitaxy" technique has recently been applied to the deposition of cadmium telluride films on (111) oriented barium fluoride substrates.(8,9) In this technique, a vertical heated quartz tube with two independent sources, cadmium telluride and cadmium, at the sealed bottom and the substrate at the top was placed in an evacuated bell-jar. When doping was desired, an indium source was introduced into the quartz tube and was heated independently of the other two sources. The substrate temperature was in the range of 480°-500°C, and the deposition rate was varied by varying the temperature of the cadmium telluride source. The important factors affecting the structural and electrical properties of the films are (a) substrate surface preparation, (b) the nucleation and growth of the first CdTe monolayers, and (c) the supersaturation during the steady growth process. By using indium as a dopant, n-type films of 6-12 μm thickness with carrier concentrations of up to about 10^{17} cm^{-3} have been deposited at rates of 1-4 μm/hr. The carrier mobility was in the range of 50-390 cm^2/V-sec, and the best mobilities were obtained for CdTe films deposited on substrates pre-nucleated with PbTe.

The sublimation of cadmium telluride in a hydrogen or an inert atmosphere has been used for the deposition of cadmium telluride films on a variety of substrates including cadmium telluride, cadmium sulfide, sapphire, etc.(10,11) The temperatures of the source and substrate are important parameters affecting the rate of deposition and the properties of the films. Alternately, the direct combination of elemental cadmium and tellurium at the substrate surface has been used for the deposition of cadmium telluride laser windows up to 15 cm^2 in area and 2 mm in thickness.(12) The stoichiometry, carrier concentration, and microstructure can be controlled by adjusting the Cd/Te molar ratio and/or the substrate temperature. The use of high substrate temperature, such as 950°C, has been found to yield windows with the best microstructure and high deposition rates.

Chemical transport technique has been used for the deposition of cadmium telluride films in gas flow and closed-tube systems. For example, epitaxial films of cadmium telluride have been deposited on the basal plane of cadmium sulfide substrates at 500°C by using hydrogen chloride as a transport agent in a gas flow system. Similar epitaxial films have also been obtained in a closed tube at lower growth rates.(13)

The electrolytic technique has been used for the deposition of cadmium telluride films on indium-tin oxide coated glass substrates at about 90°C using an acid solution of cadmium sulfate and a tellurium anode.(14) The use of low temperature is attractive; however, the grain size is relatively small, about 0.2 μm for a film of 0.2 μm thickness.

I. 2 Cadmium Telluride Solar Cells

The use of cadmium telluride for photovoltaic devices has been under investigation for nearly twenty years. The fabrication of efficient homojunction cadmium telluride solar cells is difficult for at least three reasons: (1) the junction must be shallow because of the short optical absorption length and minority carrier diffusion length in cadmium telluride, (2) the surface layer must be of low electrical resistivity to reduce the series resistance of the device, and the high dopant concentration further reduces the carrier diffusion length, and (3) the surface recombination must be minimized. The highest reported efficiency of cadmium telluride junction solar cell is about 4%.(15) MOS type solar cell prepared from chlorine-doped single crystal cadmium telluride has been reported to have an AM2 efficiency of higher than 9%.(16)

Improved conversion efficiencies have been obtained by using heterojunction structures such as $Cu_2Te/CdTe$ and CdS/CdTe. Thin film $Cu_2Te/CdTe$ solar cells have been reported by several authors. Cusano used metal foils (titanium, molybdenum, or zirconium) or n^+- CdS coated Pyrex glass discs as substrates for the deposition of n-type cadmium telluride films. The reaction between cadmium, cadmium iodide, and tellurium under reduced pressure occurs on the substrate at 450°-500°C and yields iodine-doped cadmium telluride film of about 10 ohm-cm resistivity. The cadmium telluride coated specimen is then treated briefly with a warm cuprous solution, converting the surface layer to p-type cuprous telluride of low resistivity. An important step to achieve high conversion efficiency is to compensate the surface region of the n-type cadmium telluride film by adding acceptor impurities, eliminating the donor impurities, or increasing the tellurium content near the end of the deposition process. In this type of cell, solar radiation is incident on the cuprous telluride side and is nearly all absorbed by the cadmium telluride; conversion efficiencies of about 6% have been obtained.(17)

The $Cu_2Te/CdTe$ heterojunction structure has also been prepared with the cuprous telluride layer deposited by flash evaporation.(18) The structure of the cell is: 0.04 μm Cu_2Te/10 μm n-CdTe (Cusano's method)/ 1 μm n-CdTe (vacuum evaporation)/20 μm thick Mo (substrate). The iodine-doped cadmium telluride films have carrier concentrations of 5×10^{15} to 10^{16} cm^{-3} with the highest mobility of about 30 cm^2/V-sec. It has been demonstrated that oxygen trapped at the $Cu_2Te/CdTe$ interface improves significantly the open-circuit voltage and short-circuit current of solar cells; however, the long term stability in air and short term stability at 80°C decreased. If the absorbed gas at the surface of cadmium telluride is removed by ion bombardment before the deposition of cuprous telluride, heat treatment at 150°-200°C is essential to obtain good characteristics. During heat treatment, diffusion of copper into cadmium telluride takes place and forms a thin graded n-layer by compensation. Solar cells of several square centimeter area have an average AM1 efficiency of 4.8% with $V_{oc} \sim 590$ mV and $I_{sc} \sim 13$ mA/cm^2. This type of cell has been found to show no change of V_{oc}, no sensible variation of I_{sc}, and about 2% degradation of efficiency after 1000 hrs at 70°C in air, considerably more stable than the dipped (Cusano's) cells.

The $Cu_2Te/CdTe$ structure has also been prepared with the cadmium telluride film deposited by vacuum evaporation.(19) The cadmium telluride film deposited on a CdS coated molybdenum substrate at 400°C showed a high resistivity, 10^7-10^8 ohm-cm; annealing in cadmium vapor at 350°C for 50 hrs reduced the resistivity to about 10^4 ohm-cm. The barrier layer was formed by dipping in a cuprous chloride solution. Preferred orientation along a <111> direction was obtained by selecting the angle between the substrate normal and vapor beam. Solar cells produced with well oriented CdTe layers yield open-circuit voltages up to 590 mV, whereas less oriented layers showed only 480 mV. Conversion efficiencies of up to 4.1% were obtained.

Ceramic thin film Cu_2Te/CdTe solar cells prepared by the screen printing method have been reported to have an AM1 efficiency of 8%.(20) In this method, transparent indium oxide deposited on glass followed by the deposition of a 20 μm 0.2 ohm-cm cadmium sulfide film served as a transparent ohmic contact substrate, and a cadmium telluride paste prepared from indium-doped cadmium telluride powder, cadmium chloride, and a binder was applied. This structure was heat treated in a nitrogen atmosphere to yield a cadmium telluride film of about 10 μm thickness with a grain size of 2 to 10 μm and a resistivity of 0.1-1 ohm-cm. The cadmium telluride film was then dipped for several seconds in a cuprous ion solution and heated at 200°C for 10 min, producing a p^+-Cu_2Te film at the surface. Silver paint electrode was applied to Cu_2Te, In-Ga alloy electrode was applied to CdS, and the cell was molded in a resin. Solar cells were also prepared from n-type single crystal cadmium telluride treated with a cuprous ion solution. The composition change from Cu_2Te to CdTe was found to be abrupt, and the electron voltaic effect on the cross section had a maximum in the cadmium telluride at about 1 μm from the interface. This result shows that the single crystal cell has a well-defined p-n homojunction in cadmium telluride. A similar junction structure, p^{+}-Cu_2Te/p-CdTe/n-CdTe/n-CdS, is presumably formed in the ceramic cell.

Thin film n-CdS/p-CdTe solar cells have been reported.(21) The CdTe film was deposited on molybdenum foil at 500°-700°C by the sublimation of cadmium telluride in a nitrogen-hydrogen atmosphere at a rate of about 0.3 µm/min. The deposited film is p-type with a resistivity of 10^3 to 10^4 ohm-cm, due to a small excess of tellurium, and the grain size is 5-20 µm. However, the contact between p-CdTe and molybdenum is rectifying leading to considerable series resistance and low fill factors. By evaporating about 1000 Å of copper film onto the molybdenum substrate, the copper diffuses into the cadmium telluride film during the deposition process and reduces the contact resistance. The cadmium sulfide film was deposited by vacuum evaporation at a pressure of 10^{-5} Torr and a substrate temperature of 180°C. Solar cells prepared in this manner show a conversion efficiency of 5 to 6 percent under an irradiance of 50 mW/cm^2.

Heterojunction structures between single crystalline cadmium telluride and other II-VI compounds have been investigated for solar cell purposes.(22,23) Since cadmium telluride is the only II-VI compound which can be prepared in both n-type and p-type forms and zinc telluride can only be prepared in the p-type form, the choice of the p-type member is limited to cadmium telluride or zinc telluride. The n-CdS/p-CdTe structure (lattice mismatch: 9.7%, expansion mismatch: 9%) has been studied in detail; cadmium sulfide serves as a window and minimizes the surface recombination of light-generated carriers, and the maximum theoretical conversion efficiency is 17%. N-CdS/p-CdTe heterojunctions have been prepared by close-spaced chemical transport of p-CdTe films onto single crystal n-CdS, by vacuum evaporation of n-CdS films onto single crystal p-CdTe, by solution spraying of n-CdS films onto single crystal p-CdTe, and by the epitaxial deposition of n-CdS films on single crystal p-CdTe. The close-spaced transport of p-CdTe films of 15-400 ohm-cm resistivity onto single crystal n-CdS at 480°C has produced solar cells with a quantum efficiency of 0.85 and a conversion efficiency of 4%.(11,23) The vacuum evaporation of low resistivity n-CdS films onto a p-type single crystal CdTe of 3-130 ohm-cm resistivity grown by the Bridgman technique has produced solar cells with a quantum efficiency of 0.82 and a conversion efficiency of 7.9%.(24) Solar cells prepared by the deposition of CdS films by spray pyrolysis on single crystal CdTe are similar to those prepared by evaporation.(25) Solar cells with a conversion efficiency of 12% have been claimed by using the sublimation of cadmium sulfide on the (111) surface of p-type cadmium telluride crystal grown by the Bridgman technique.(26) In addition to n-CdS/p-CdTe heterojunction structures, p-ZnTe/n-CdTe structures (lattice mismatch: 5.8%) have also been prepared by close-spaced chemical transport technique; however, their quantum efficiency was only about 2%.(27) Available data on heterojunction structures indicate no serious loss of photovoltaic performance in transferring from a single crystal to thin films. Furthermore, the commonly accepted assumption that lattice mismatch and high quantum efficiency are mutually exclusive is not necessarily valid; a high local field at the interface can effectively prevent recombination through interface states and permit a large quantum efficiency of the cell.

I. 3 Technical Approaches

The overall objective of this program is to demonstrate the feasibility of producing high efficiency thin film cadmium telluride solar cells. The technical approaches selected to fulfill this objective 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.

During the course of this program, an apparatus for the chemical vapor deposition of cadmium telluride has been designed and constructed. More than two hundred experiments on the deposition of cadmium telluride films on several types of substrates have been carried out, and their structural, electrical, and photovoltaic properties evaluated. From these experiments, the problems associated with the deposition of cadmium telluride films for photovoltaic applications have been identified, and possible approaches to overcome these problems suggested. The experimental procedures and results are discussed in the following sections.

II. Selection and Preparation of Substrates

The substrates for the deposition of cadmium telluride films for solar cell purposes must be of low cost and must possess certain electrical, chemical, and mechanical properties. The substrate must provide a low resistance electrical contact to the active layer, must be inert under the conditions used for the deposition of cadmium telluride films, and must be mechanically compatible with the active layer over a wide range of temperature. In addition, substrates with high electrical conductivity are preferred so that they may serve as an ohmic contact to the solar cell. The structural properties of the substrate should also be considered since the microstructure and crystallographic properties of cadmium telluride films depend, to a great extent, on the structural properties of the substrate.

Because of the chemical environment in the deposition of cadmium telluride films, the choice of substrates is rather limited. Graphite appears to be an economical substrate for large area solar cells. Several types of graphite, such as grade PLC and PEL 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, $5.5 \times 10^{-6}\,^{o}C^{-1}$. Graphite is chemically inert under the conditions used for the deposition of cadmium telluride. Also, graphite has high thermal and electrical conductivities and may be used as an ohmic contact to the solar cell. However, the density of low-cost graphite is 1.65-1.75g/cm^{-3} (theoretical density of graphite: 2.2g/cm^{3}), corresponding to a porosity of 20-25%. Consequently, the surface of graphite has a high concentration of pits, and uniform nucleation of cadmium telluride cannot be expected. To provide a homogeneous surface, a thin layer of an impervious material, such as carbon, silicon, or tungsten, was deposited on graphite substrates. In addition to coated graphite, mullite was also used as a substrate to facilitate the characterization of electrical properties of cadmium telluride films.

POCO PLC or PEL graphite plates of 1-1.5 mm thickness were used as the starting material. The deposition of carbon, silicon, and tungsten was carried out, respectively, by the pyrolysis of propane, the thermal reduction of trichlorosilane, and the thermal reduction of tungsten hexafluoride using the apparatus shown schematically in Fig. 3. The flow of various gases, such as hydrogen, propane, and tungsten hexafluoride, was directed by using appropriate valves and measured with flowmeters. Trichlorosilane was introduced into the reaction tube by bubbling hydrogen at a measured rate through the liquid. A Millipore filter was used to remove any solid particles present in the reactant gas. The reaction tube was made of fused silica and was of 55 mm ID. The graphite substrates were supported on a graphite susceptor, and the susceptor was heated externally by an rf generator. Prior to the deposition process, the substrates were first heated in hydrogen at 1100-1200°C to remove the surface contaminations.

Carbon was deposited on graphite substrates at 1100°-1150°C using argon at a flow rate of 8ℓ/min, and the deposition rate can be varied over a wide range by controlling the flow rate of propane. For example, the deposition rate of carbon was about 0.3 μm/min at a propane flow rate of 20 mℓ/min and may be increased to about 0.8 μm/min by increasing the flow rate of propane to 200 mℓ/min. The density of deposited carbon, determined by the floating equilibrium method, is 2.14-2.15 g cm^{-3}; the carbon deposited at lower rates had slightly higher density. Thus, pyrolytic carbon is con-

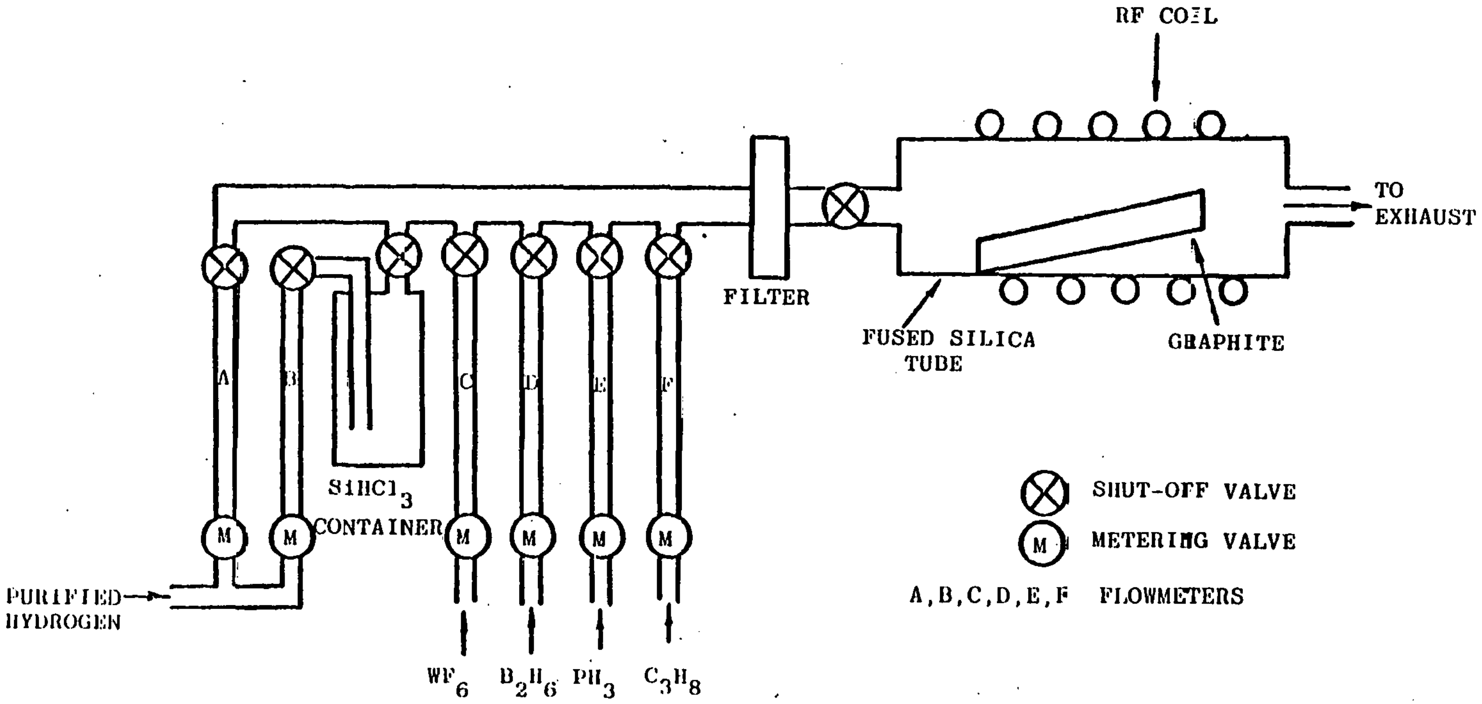


Fig. 3 Schematic diagram of the apparatus for the deposition of carbon, silicon, and tungsten on graphite.

siderably more impervious than graphite.

Silicon was deposited on graphite at 1100°C by using hydrogen and trichlorosilane at flow rates of 1 and 0.02 moles/min, respectively. The deposition rate was about 1 μm/min; the crystallite size was dependent on the thickness, 2-3 μm for a layer of 3-5 μm thickness. X-ray diffraction examinations indicate that the deposit is essentially polycrystalline with no appreciable preferred orientations.

Tungsten was deposited on graphite using a hydrogen flow rate of 25 ℓ/min; this relatively high flow rate was used to minimize the gas phase nucleation and the thickness variations of the deposit. The flow rate of tungsten hexafluoride was 30 mℓ/min, and the substrate temperature was in the range of 450-500°C. Tightly adherent layers of tungsten were obtained in all cases at rates of up to 0.5 μm/min. The average size of crystallites in tungsten films of 2-5 μm thickness deposited at 500°C is 1-2 μm, and these films show a strong (100) preferred orientation. At higher substrate temperatures, the gas phase nucleation becomes pronounced, and the deposited films contain non-adherent large crystallites from gas phase reactions.

Although coated graphite substrates provide a relatively homogeneous surface for the nucleation and growth of cadmium telluride, these substrates do not form low resistance ohmic contacts with n- and p-type cadmium telluride films deposited in this program. 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 work 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 $\exp(-C\phi^{1/2}t)$, where ϕ is the barrier height and t its thickness (t is proportional to $N^{-1/2}$, 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 films. The group III elements, such as aluminum, indium, and thallium, were deposited on W/graphite substrates by vacuum evaporation. Indium was also deposited in-situ just prior to the deposition of cadmium telluride films by the reaction of indium and hydrogen chloride in a hydrogen atmosphere. Indium was 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:

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

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

The work function of p-type cadmium telluride is higher than 5 eV, and common metals are not suitable as ohmic contacts. Thus, it is necessary to produce a heavily doped region in cadmium telluride adjacent to the contact metal. Antimony and bismuth were deposited on W/graphite by vacuum evaporation for this purpose; the dissolution of antimony or bismuth in cadmium telluride is expected to yield a heavily doped region at the interface. In addition, p-type lead telluride and bismuth telluride were synthesized from the elements and their films deposited on tungsten/graphite as substrates for the deposition of p-type cadmium telluride.

III. Chemical Vapor Deposition of Cadmium Telluride Films

The chemical vapor deposition technique in a gas flow system has been used extensively for the deposition of semiconductor films. This technique has two distinct advantages: (1) a wide range in thickness from a fraction of a micrometer to hundreds of micrometers can be achieved and controlled, and (2) the dopant concentration and distribution in the deposit can be controlled to an extent not obtainable by other techniques. It is essential that the chemical reaction is predominately heterogeneous taking place on the substrate surface. In contrast, volume reaction results in the formation of molecular clusters of random orientations in the space surrounding the substrate, and the deposition of these clusters on the substrate will produce non-adherent deposit. Furthermore, the by-products of the reaction must be volatile at the processing temperature to insure high purity of the deposit.

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

(1) Reactions between elemental cadmium and tellurium

$$2\ \mathrm{Cd(g)} + \mathrm{Te_2(g)} \rightarrow 2\ \mathrm{CdTe\ (s)}$$

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

$$2\ \mathrm{H_2\ (g)} + 2\ \mathrm{CdI_2\ (g)} + \mathrm{Te_2\ (g)} \rightarrow 2\ \mathrm{CdTe\ (s)} + 4\ \mathrm{HI\ (g)}$$

The apparatus used for the deposition of cadmium telluride films is shown schematically in Fig. 4. It consists of two parts: a gas flow control panel and a reaction tube containing cadmium (or cadmium iodide), tellurium, and substrate at appropriate temperatures. On the gas control panel, flowmeters and valves are used to control the flow of hydrogen, hydrogen iodide,

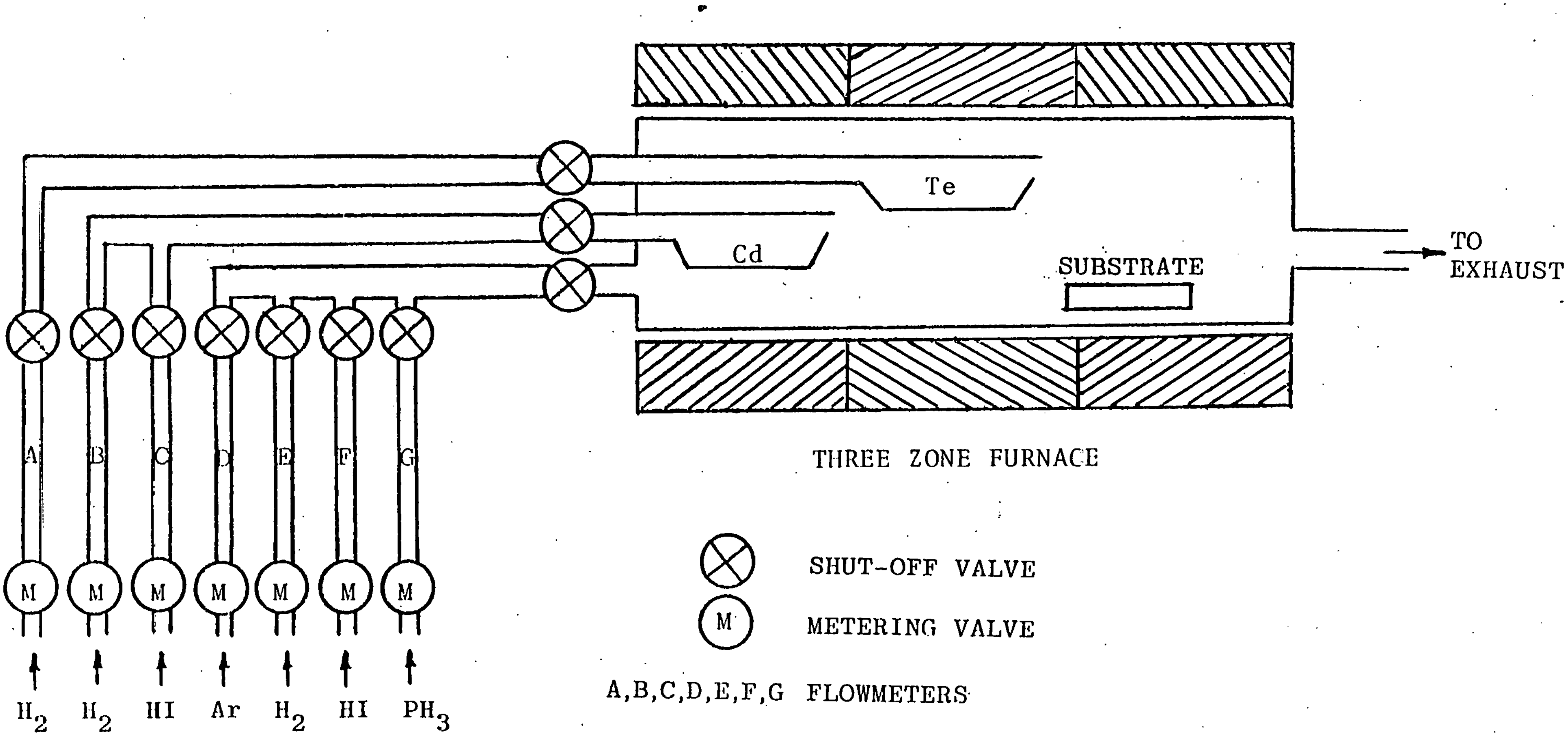


Fig. 4 Schematic diagram of the apparatus for the deposition of cadmium telluride films.

and phosphine (a p-type dopant). Hydrogen is used to carry cadmium (or cadmium iodide) and tellurium vapors into the reaction tube. The fused silica reaction tube is of 55 mm ID and 59 mm OD; the use of a relatively large diameter reaction tube facilitates the preparation of large area cadmium telluride films of uniform properties. The reaction tube is held in a three-zone resistance-heated furnace with each zone separately heated and controlled.

To carry out the deposition of cadmium telluride by direct combination, a cadmium container, a tellurium container, and the substrate are placed in the appropriate temperature zones. Hydrogen is introduced into the cadmium and tellurium containers to carry the reactants to the substrate surface where the chemical combination takes place depositing cadmium telluride. The initial partial pressures of cadmium and tellurium at the substrate surface, P^o_{Cd} and $P^o_{Te_2}$, may be estimated from the temperatures of cadmium and tellurium and the flow rates of hydrogen through the sources and the reaction tube. When $P^o_{Cd}(P^o_{Te_2})^{1/2}$ is higher than the dissociation constant of cadmium telluride at the substrate temperature, K_{CdTe}, the deposition of cadmium telluride takes place so that the partial pressures of cadmium and tellurium are reduced to P_{Cd} and P_{Te_2}, respectively, in order to satisfy the relation

$$P_{Cd}(P_{Te_2})^{1/2} = K_{CdTe}$$

When P_{Cd} and P_{Te_2} are lower than the equilibrium vapor pressures of cadmium and tellurium at the substrate temperature, excess cadmium and tellurium should not condense, and the stoichiometry of the deposit could be maintained. The deposition rate of cadmium telluride is determined by the degree of supersaturation of cadmium and tellurium at the substrate surface and is given by:

$$n_{CdTe} = (P^{o}_{Cd} - P_{Cd}) \ V / RT$$

$$= (P^{o}_{Te_2} - P_{Te_2}) \ V / RT$$

where V is the total gas flow rate. Thus, the reactant composition and substrate temperature are important parameters determining the deposition rate of cadmium telluride.

III. 1 Initial Stage of Deposition

The deposition of cadmium telluride films on W/Graphite, mullite, and other inert substrates by the reaction of cadmium and tellurium has been studied in 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. It is generally accepted that films grown by vapor deposition techniques consist of isolated nuclei at small thicknesses and that these nuclei act as growth centers. On a homogeneous substrate surface, their density is related to the substrate surface topography, the substrate-deposit interaction, the substrate temperature, and the reactant composition. For example, at a given reactant composition, the density of initial nuclei decreases with increasing substrate temperature. The subsequent film growth proceeds by the enlargement of crystallites around these nuclei, rather than by the generation of fresh nuclei. The coalescence of all adjacent islands produces a completely continuous structure. The thickness at which the film becomes continuous is related to the density of initial nuclei and the relation of growth rates in the thickness and lateral directions of the crystallites. At low densities of nucleation, continous films can only be obtained at relatively large thicknesses.

The initial stage of deposition of cadmium telluride on a tungsten/graphite substrate at 500°C is shown at two magnifications in Fig. 5, 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. 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. The pinhole density can be reduced by carrying out the deposition at lower temperatures; however, no adherent films can be obtained at temperatures below about 450°C.

The nucleation and growth of cadmium telluride films on other inert substrates, such as mullite and carbon/graphite, are very similar to those on tungsten/graphite substrates. The deposition of large area pinhole free films is very difficult.

III. 2 Effects of Reactant Composition

When cadmium telluride films are deposited by the direct combination of the elements at the heated substrate surface, the Cd/Te molar ratio in the reactant mixture should not affect the stoichiometric composition of the deposit as long as the partial pressures of the excess cadmium or tellurium is below their equilibrium vapor pressures at the substrate temperature. To determine the validity of this reasoning, a series of deposition experiments on mullite and tungsten/graphite substrates were

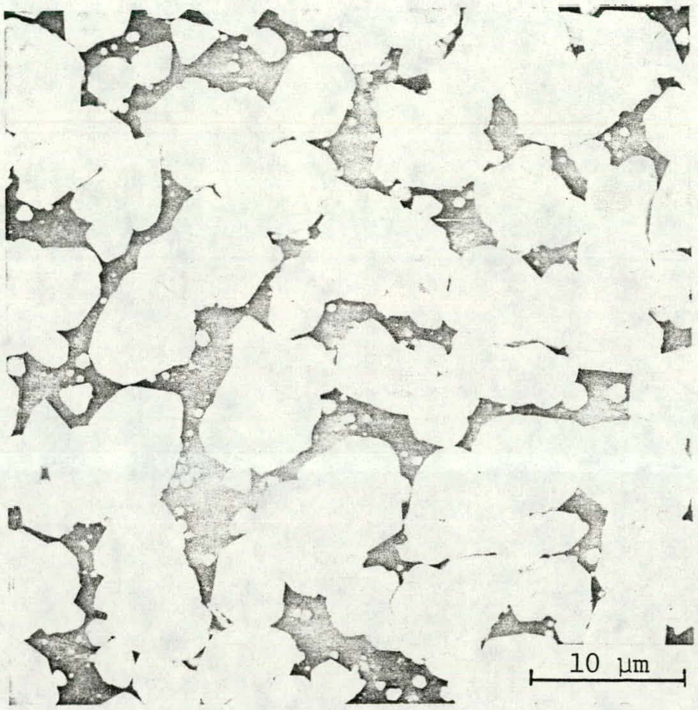


Fig. 5 The initial stage of deposition of cadmium telluride about 2 µm thickness, on a tungsten/graphite substrate at 500°C.

carried out using a wide range of Cd/Te molar ratio in the reactant mixture. The substrate was maintained at 500°-550°C, the total flow rate of hydrogen was 2ℓ/min, and the partial pressure of cadmium in the reactant mixture was 0.4 Torr. The partial pressures of tellurium (Te_2) were 0.135, 0.16, 0.2, 0.25, and 0.3 Torr, corresponding to Cd/Te molar ratios of 1.5, 1.25, 1.0, 0.8, and 0.67, respectively. At 500°C, the equilibrium partial pressures of cadmium and tellurium (Te_2) from cadmium telluride are 3.9×10^{-4} and 1.95×10^{-4} Torr, respectively, while the equilibrium vapor pressures of cadmium and tellurium are 14 and 0.7 Torr, respectively. Since the partial pressures of cadmium and tellurium in the reactant mixture are lower than their equilibrium vapor pressures, no free cadmium or tellurium should condense in the deposited films.

The deposition rate of cadmium telluride films, determined directly from vertical cross-sectioned surfaces, was found to depend strongly on the Cd/Te molar ratio in the reactant mixture; the use of an excess of cadmium decreases the deposition rate while excess tellurium increases the deposition rate. The results are shown in Fig. 6, where the deposition rate increased from about 0.1 μm /min at a Cd/Te molar ratio of 1.25 to about 0.55 μm/min at a Cd/Te molar ratio of 0.8. This strong dependence of deposition rate on the reactant composition may be due to the low sticking coefficient of cadmium.

All deposited cadmium telluride films are tightly adherent to the substrate. They are polycrystalline, and the as-deposited surfaces were examined with optical and scanning electron microscopes to determine their microstructure. Figure 7 shows the scanning micrographs of the five cadmium telluride films deposited at 500°C using various Cd/Te molar ratios. As the Cd/Te molar ratio decreases, the thickness of cadmium

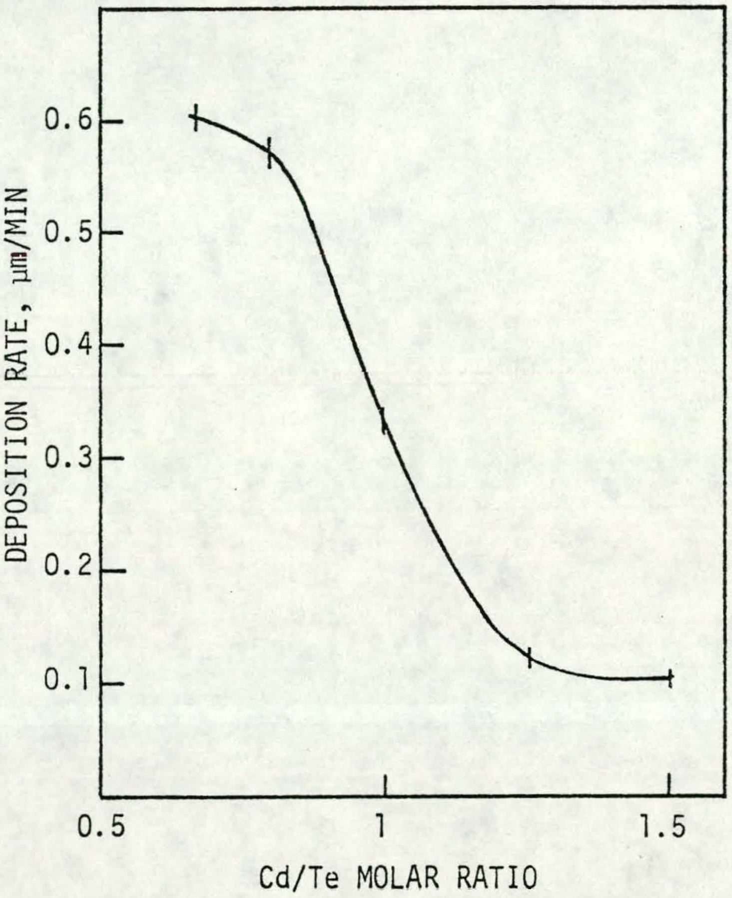
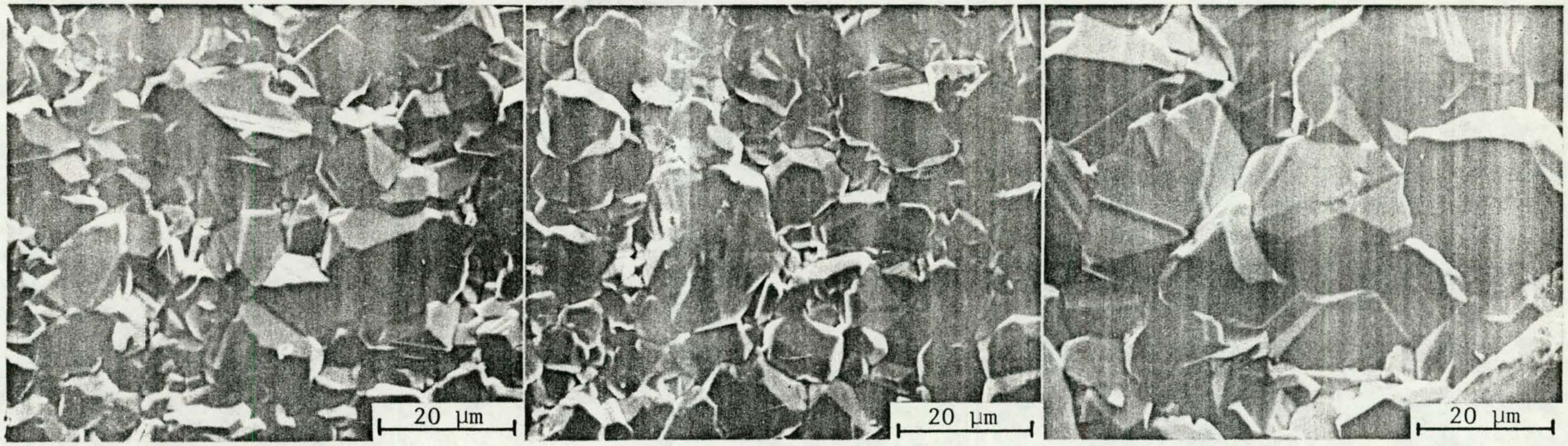


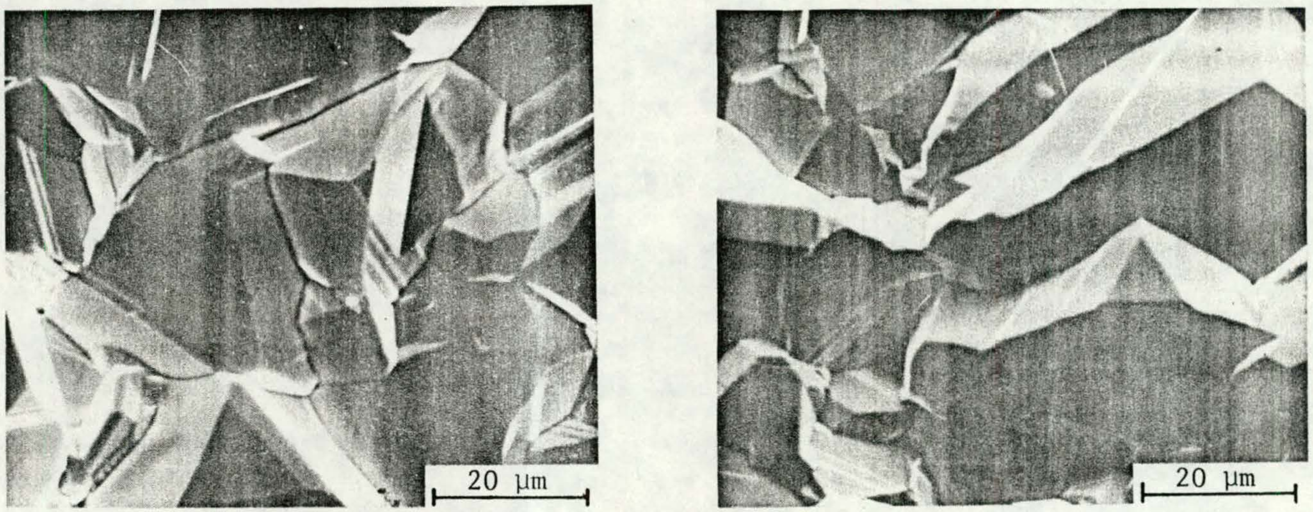
Fig. 6 Deposition rate of cadmium telluride films on W/graphite substrates at 500^{o}C as a function of Cd/Te molar ratio in the reactant mixture.



Cd/Te = 1.5, 6 µm

Cd/Te = 1.25, 7 µm

Cd/Te = 1.0, 20 µm



Cd/Te = 0.8, 34 µm

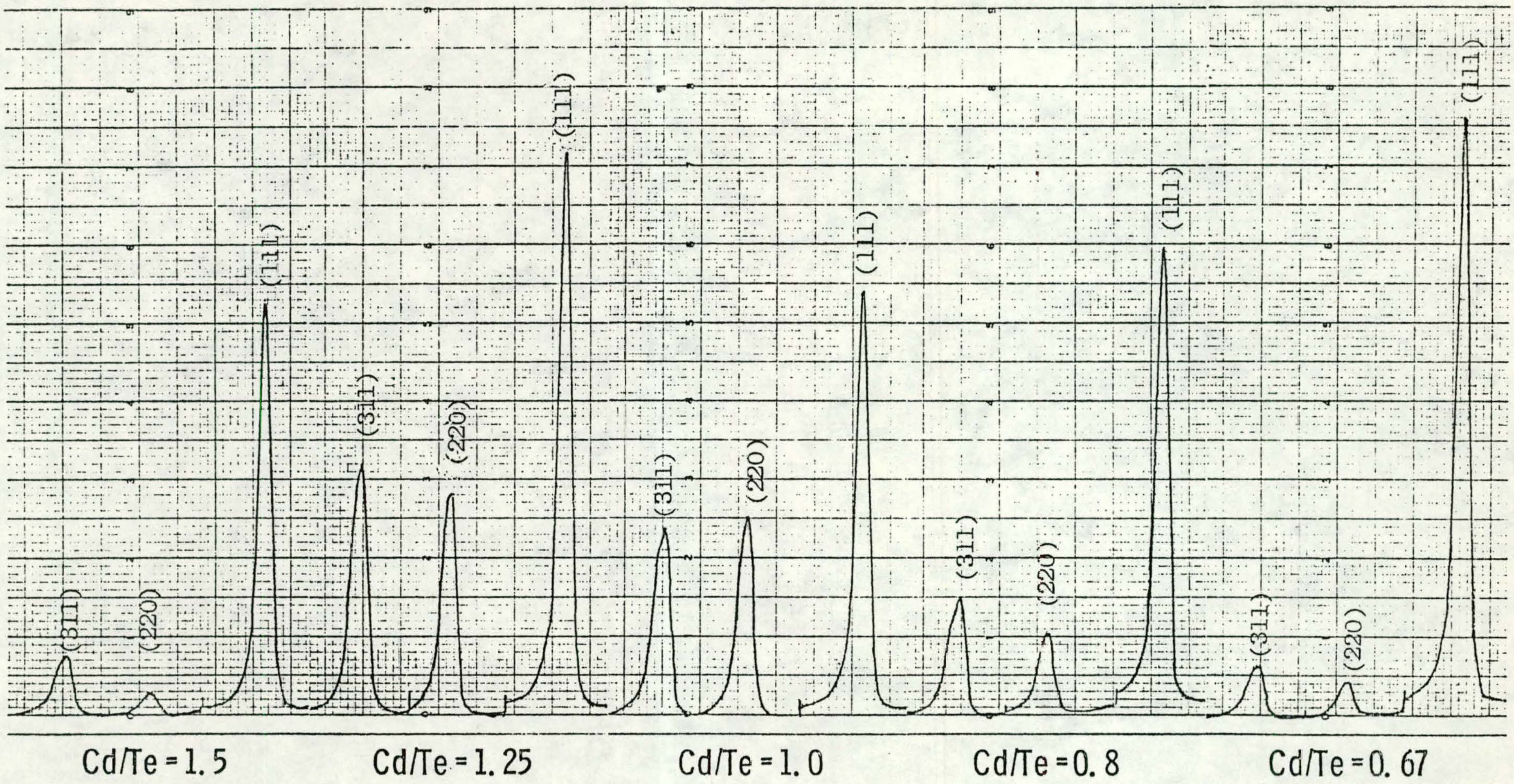
Cd/Te = 0.67, 36 µm

Fig. 7 Scanning electron micrographs of cadmium telluride films deposited on W/graphite substrates at 500°C using different Cd/Te molar ratios in the reactant mixture.

telluride film increases, and the average grain size also increases. In addition to thickness, the substrate temperature is also an important factor determining the grain size in the films. The grain size increases with increasing temperature; however, the surface becomes relatively rough due to the dependence of growth rate on crystallographic orientation. Further, the pinhole problem becomes more pronounced because of the decrease of nucleation rate with increasing temperature.

The crystallographic properties of cadmium telluride films deposited on tungsten/graphite substrates have been examined by the x-ray diffraction technique. Polycrystalline cadmium telluride powder of random orientations is known to show three strong diffraction peaks associated with {111}, {220}, and {311} reflections with d values of 3.742, 2.290, and 1.954 Å and relative intensities of 100, 62, and 28, respectively. The diffraction spectra of the cadmium telluride films, obtained by scanning 2θ in the range of 20-60°, are shown in Fig. 8. All films are essentially polycrystalline. However, films deposited with high Cd/Te molar ratios exhibited weak cadmium reflections indicating the presence of cadmium inclusions.

The X-ray diffraction technique is of limited use here since it cannot furnish accurate information on the composition of cadmium telluride films deposited using various Cd/Te molar ratios in the reactant mixture. Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) techniques were used by Dr. Larry Kazmerski at SERI to determine the difference in the composition of these cadmium telluride films. In the AES technique, the ratio of the 337 eV Cd peak to the 483 eV Te peak was used as the reference. In the SIMS technique, the ratio of the Cd^{114} peak to the Te^{130} peak was used as the reference. A single crystal cadmium



● WEAK CADMIUM (101) REFLECTION PRESENT WHEN Cd/Te 1

Fig. 8 X-ray diffraction spectra of cadmium telluride films deposited on W/graphite substrates at 500° using different Cd/Te molar ratios in the reactant mixture.

telluride was used as a standard in both cases. The results of the average of 125 data points from each specimen are summarized in Table I. In the cadmium telluride film prepared from a reactant mixture with Cd/Te=1, the AES and SIMS data are very similar to those of the single crystalline material. At a Cd/Te molar ratio of 1.25, the cadmium telluride film contain an excess of cadmium, and at a Cd/Te molar ratio of 0.8, the cadmium telluride film contain an excess of tellurium, as shown by both AES and SIMS data. Thus, the deductions concerning the stoichiometric composition of cadmium telluride films made from vapor pressure considerations are incorrect, and the reactant composition is an important factor determining the composition of deposited cadmium telluride films.

Hall mobility and resistivity measurements were attempted at room temperature on cadmium telluride films deposited on ceramic substrate using various Cd/Te molar ratios without intentional doping. The van der Pauw method was used, and the four contacts to the periphery of the specimen were made by evaporating indium through a metal mask. Lateral resistances were measured with current through all six possible combinations of contact pairs. In all cases, the measured dark resistances were extremely high, and the results were inconsistent. More consistent results were obtained by carrying out the resistance measurements under AM1 illumination. The measured resistivity, as shown in Fig. 9, are in the range of 2-6 x 10^4 ohm-cm. Attempts were also made to measure the electrical resistivity of cadmium telluride films in the thickness direction on tungsten/graphite substrates. Since the CdTe/W interface is rectifying, and the CdTe/In interface may also have a high resistance, the measured resistivities, 3-10 x 10^3 ohm-cm represent the upper limit of the electrical resistivity of cadmium telluride films. These results indicate that the high lateral

Table I AES and SIMS Analysis (Average of 125 Data Points) of Cadmium Telluride Films deposited by using various Cd/Te Molar Ratios.

Cd/Te MOLAR RATIO IN REACTANT	AES (377 eV Cd/483 eV Te)	SIMS (Cd^{114}/Te^{130})
1.67	1.38	2.1
1.25	1.26	1.4
1.0	1.22	1.08
0.8	1.18	0.9
0.67	1.18	0.88
SINGLE CRYSTAL	1.20	1.15

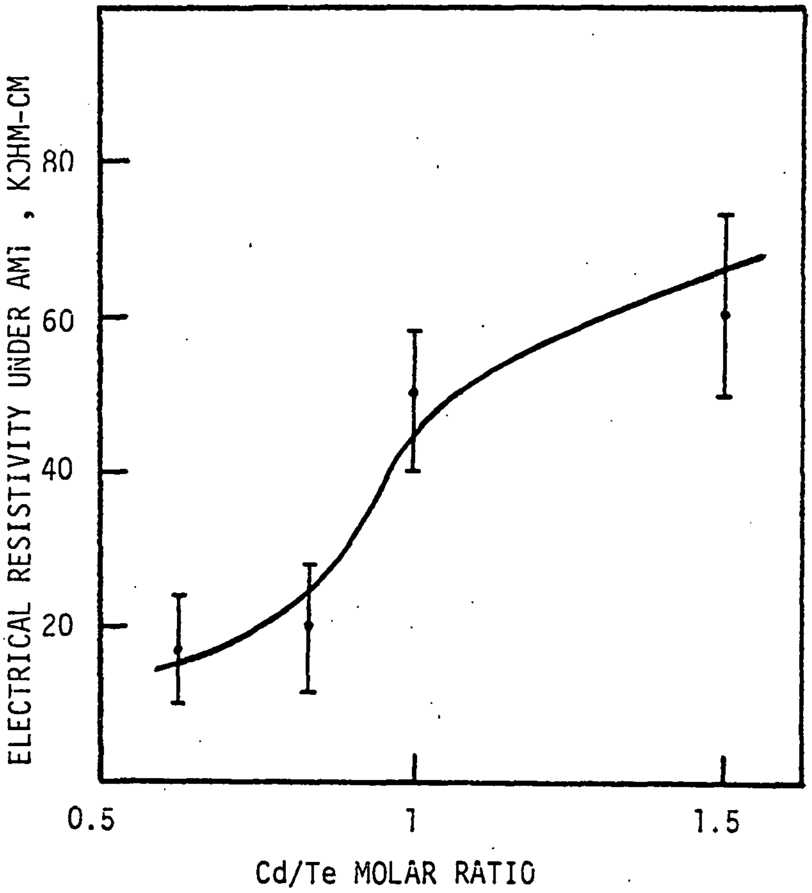


Fig. 9 Lateral resistivity of cadmium telluride films as a function of Cd/Te molar ratio measured under AM1 conditions.

resistivity in cadmium telluride films are contributed mostly by the potential barrier at grain boundaries.

III. Cadmium Telluride Films by the Reaction of Cadmium Iodide and Tellurium

The deposition of cadmium telluride films by the reaction of cadmium iodide and tellurium in a hydrogen atmosphere was carried out in an apparatus similar to that shown in Fig. 3; the cadmium container in the deposition apparatus was replaced by a fused silica boat containing C.P. grade cadmium iodide. 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.

IV. Deposition and Characterization of n-type Cadmium Telluride Films

The deposition of n-type cadmium telluride films was carried out by the direct combination of the elements using hydrogen iodide or indium as a dopant. During the early stage of this work, carbon/graphite, silicon/graphite, W/graphite were used as substrates for the deposition process. In all cases, the CdTe/substrate interface was found to be rectifying, as shown by the high dark resistance of Schottky barrier fabricated from these films. Further, a significant fraction of the Schottky barriers has been found to be shorted due to the presence of pinholes in the films. To overcome the interface rectification problem, Aℓ/W/graphite, In/W/graphite, and CdS/W/graphite substrates were used.

IV. 1 Cadmium Telluride Films on Aℓ/W/Graphite Substrates

Aluminum films of about 1 μm thickness were deposited on W/Graphite substrates by evaporation. The deposition of n-type cadmium telluride films was carried out in the temperature range 500^o - 600^oC, and the concentration of hydrogen iodide in the reactant mixture was 0.1-0.2% (cadmium telluride is etched when the concentration of hydrogen iodide in the reactant mixture exceeds about 0.5%). The specimen was heated at 675^oC (m.p. of Aℓ: 660.2^oC) 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.

IV. 2 Cadmium Telluride Films on In/W/Graphite Substrates

Indium films of 1-2 μm thickness were deposited on W/graphite substrates by evaporation or by the in-situ disproportionation of indium monochloride just prior to the deposition process. The use of the indium interlayer has been found to provide an ohmic contact to the substrate. Further, the use of an indium interlayer, a liquid at the temperature used for the deposition process, also facilitates the nucleation of cadmium telluride. X-ray diffraction examinations indicate that the deposited films are also polycrystalline with no preferred orientations. The carrier concentration in the film has been calculated to be $(1\text{-}3) \times 10^{13}$ cm^{-3} from differential capacitance measurements. The carrier concentration in cadmium telluride films cannot be further increased by increasing the flow rate of hydrogen iodide in the reactant mixture. The electrical resistivity of cadmium telluride films deduced from the forward characteristics of Schottky barriers is $(3\text{-}8) \times 10^{3}$ ohm-cm. The carrier mobility cannot be measured directly because of the presence of conducting substrate. Similar films deposited on mullite substrate have carrier mobilities in the range of 20-30 cm^2/V-sec.

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.

Schottky barriers have been prepared from many cadmium telluride films deposited on In/W/Graphite substrates by evaporating silver dots of 0.2 - 2 mm^2 area onto the surface of the specimen. Figure 10 shows the

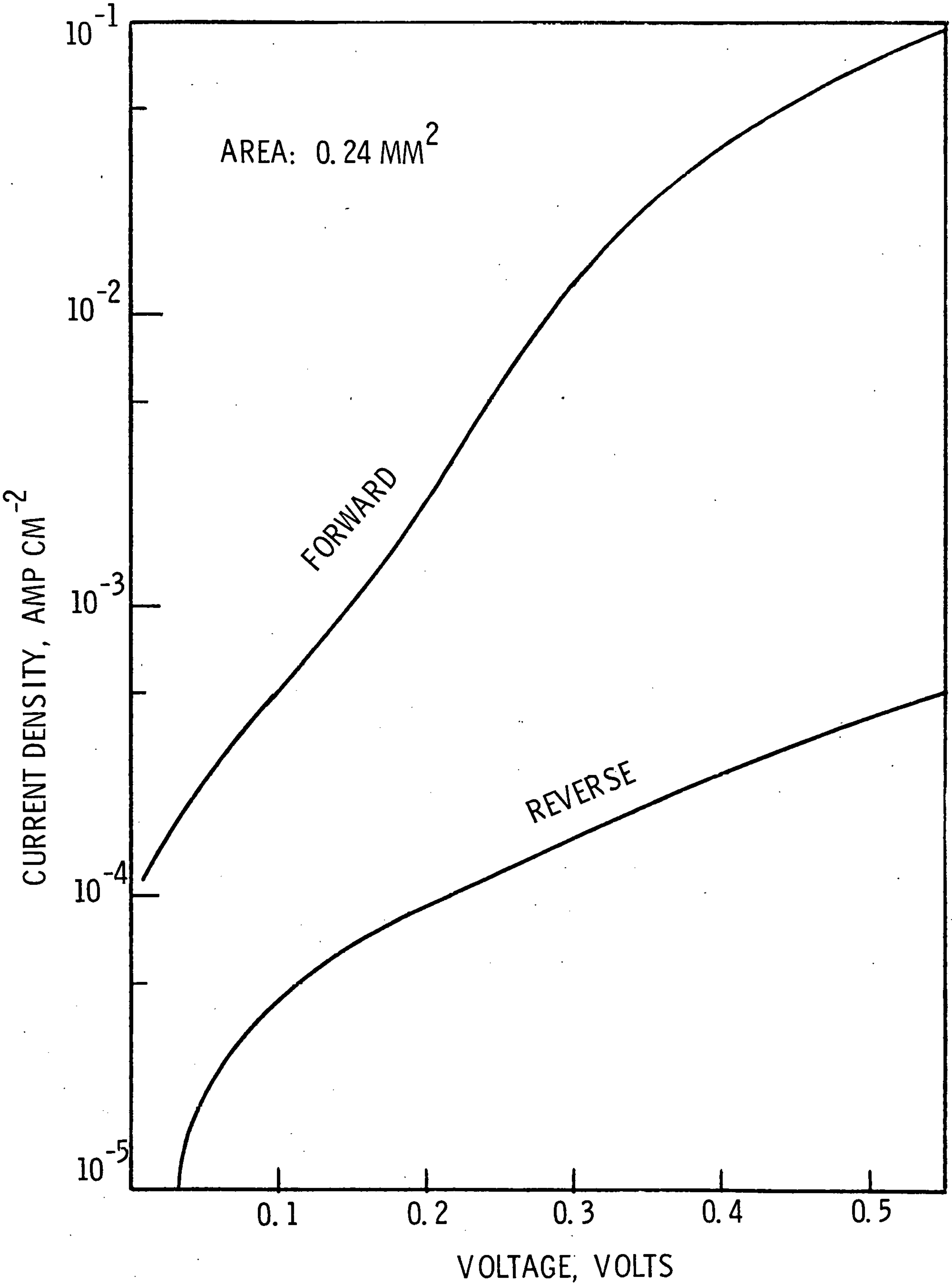


Fig. 10 Dark current-voltage characteristics of a Ag/n-CdTe/In/W/graphite structure of 0.24 mm^2 area.

dark current-voltage of a Schottky barrier of 0.24 mm^2 area. Nearly all Schottky diodes are characterized by high dark current due presumably to grain boundary shunting effects. The barrier height in Ag/CdTe(I-doped)/In/W/Graphite structures, measured by the photoresponse method, is about 0.76 eV. The effective intragrain minority carrier diffusion length in cadmium telluride films of the Schottky barrier structure, measured by the scanned electron beam method, is in the range of 0.8   1.8 μm.

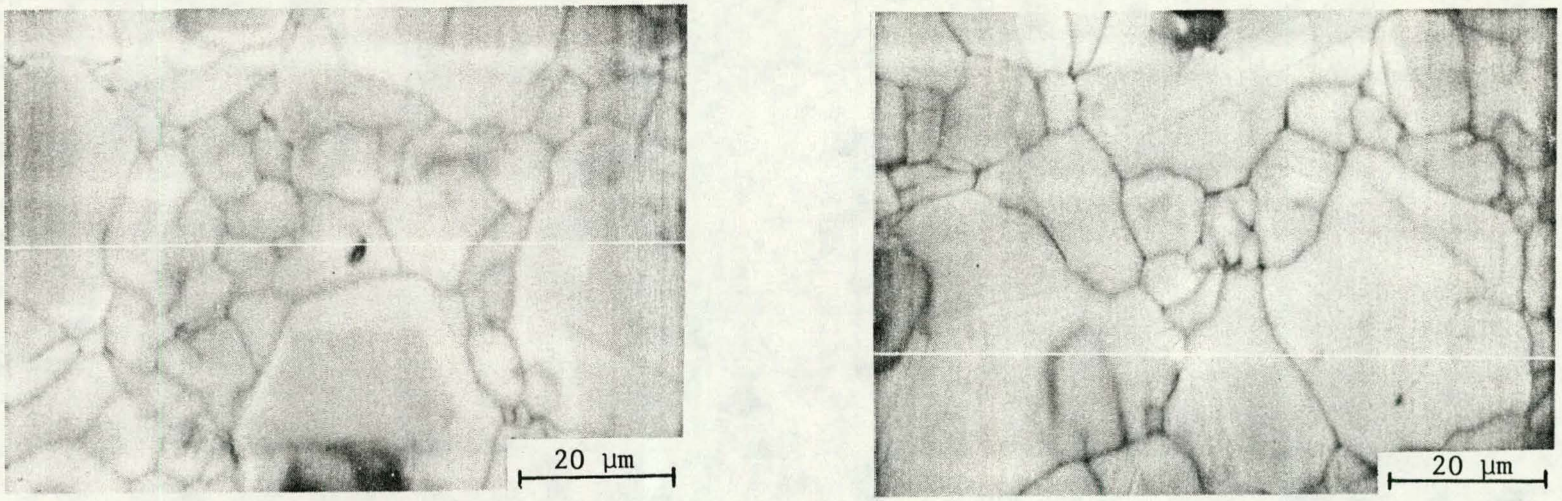
A number of Schottky barrier solar cells of 1 cm^2 area have been prepared in the following manner. A gold or silver film of 60 - 80 Å thickness was evaporated onto the surface of cadmium telluride films deposited on In/W/Graphite substrates under a pressure of less than 10^{-6} Torr. The grid contact, 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 - 15 mA/cm^2; however, the low open-circuit voltage, about 300 mV, and low fill factor, 36 - 42%, 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.

The effects of grain boundaries in thin film cadmium telluride Schottky barrier solar cells were studied by the electron beam induced current techniques (EBIC). Figure 11 shows two typical EBIC micrographs using 20 keV electrons, where the reduced current collection at grain boundaries is apparent. Also shown are the scans of the induced current signal across the surface of the solar cells along positions indicated by the horizontal lines in the EBIC photographs. The signals are considerably reduced at grain boundaries, as expected. Attempts to reduce the grain boundaries effects by thermal oxidation were not successful.

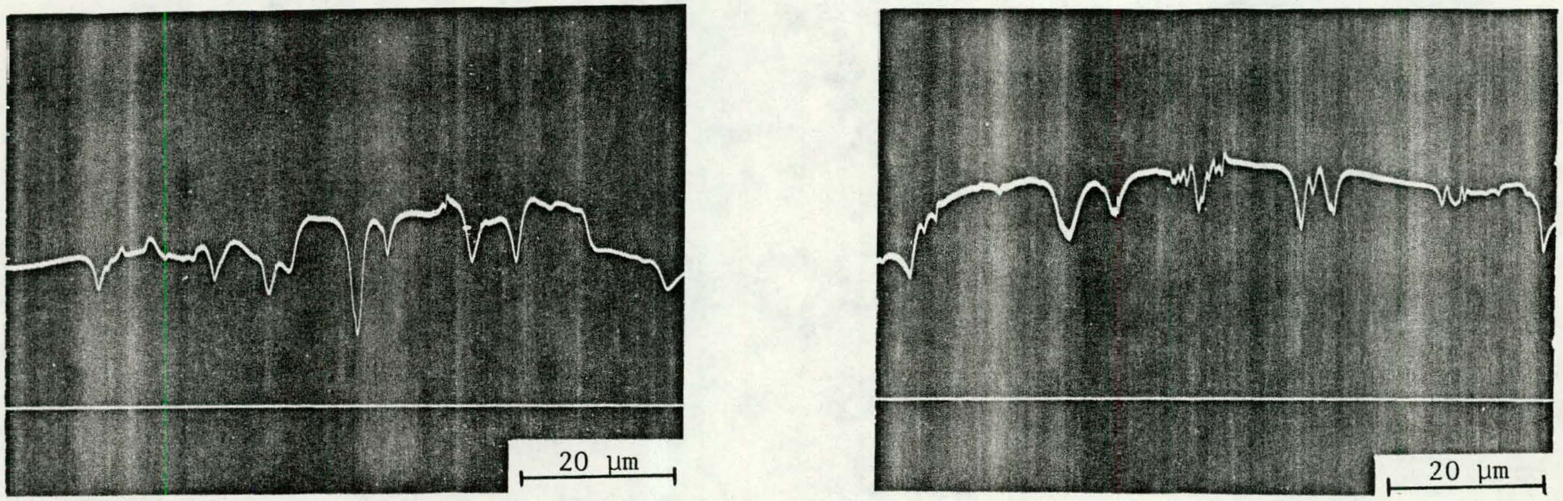
Auger profile studies by Dr. Kazmerski of SERI have shown that in CdTe/In/W/graphite structures, indium from the interface has essentially all diffused into the cadmium telluride film. Cadmium telluride films were also deposited on Tℓ/W/graphite substrates. The CdTe/Tℓ interface is also ohmic; however, the diffusion of thallium into the cadmium telluride film remains to be a problem.

IV. Cadmium Telluride Films on CdS/W/Graphite Substrates

Since low resistivity n-type cadmium telluride forms low resistance ohmic contact with n-type cadmium telluride, n-type cadmium sulfide films were deposited by the reaction of cadmium and hydrogen sulfide. The deposited cadmium sulfide has a room temperature electron concentration of about 2×10^{18} cm^{-3} and a carrier mobility of 10 cm^2/V-sec. Schottky barriers prepared from n-CdTe/n-CdS/W/graphite structures were also found to show high dark current, Fig. 12, due to grain boundary effects.



EBIC MODE



SCAN OF BEAM INDUCED CURRENT

Fig. 11 EBIC micrograph and induced current scan across the surface of a Ag/n-CdTe/In/W/graphite solar cell.

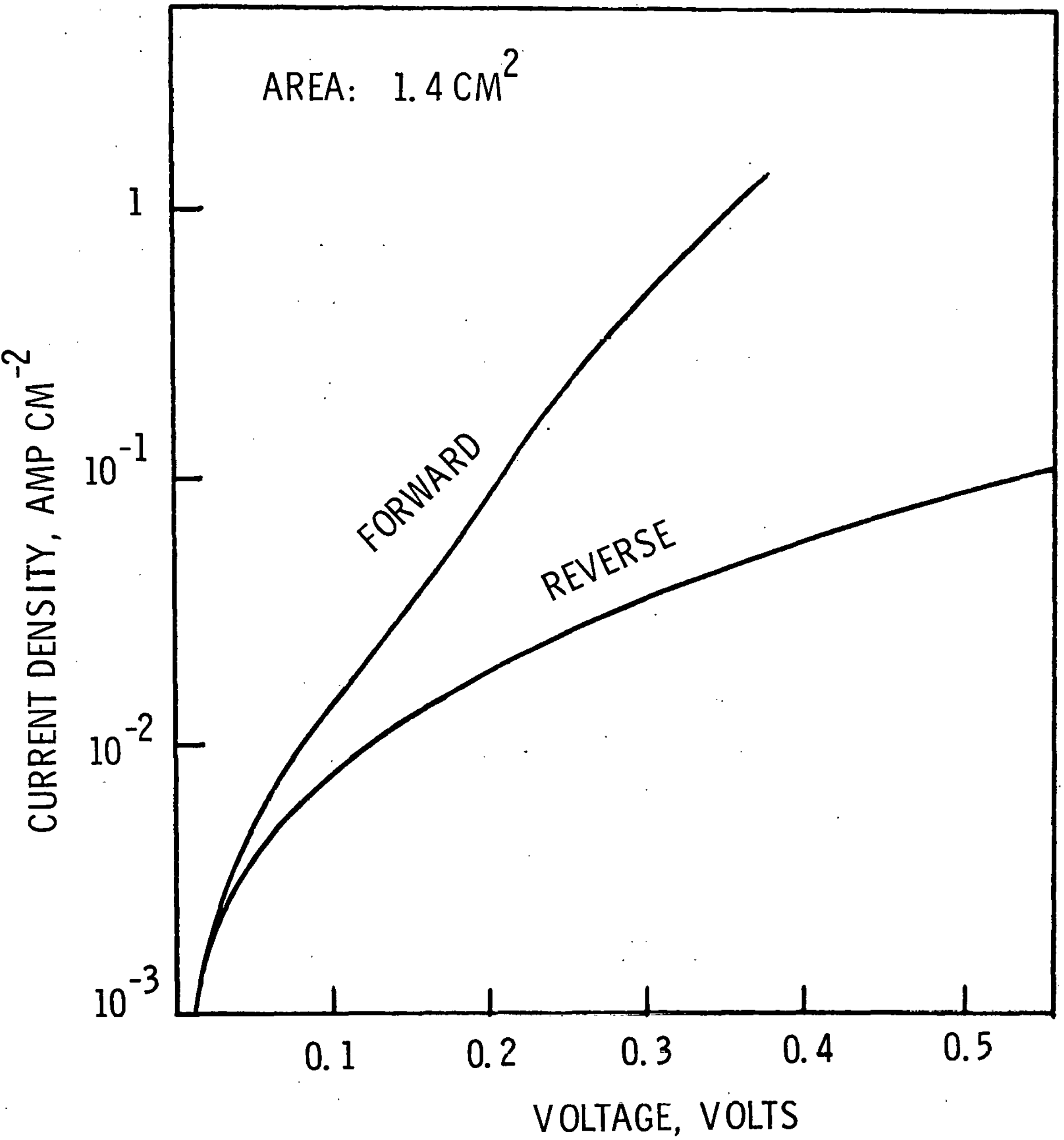


Fig. 12 Dark current-voltage characteristics of a Ag/n-CdTe/Cds/W/graphite structure of 1.4 cm^2 area

V. Deposition and Characterization of p-type Cadmium Telluride Films

A series of experiments on the deposition of p-type cadmium telluride films on foreign substrates have been carried out. Since the selection of the contact material for p-type cadmium telluride is difficult since it should have a larger work function, the CdTe/substrate interface resistance could be reduced to a tolerable level by producing a region of high carrier concentration in cadmium telluride at the interface region. Antimony and bismuth, known to be acceptors in cadmium telluride, are suitable candidates for the contact material. Sb/W/graphite and Bi/W/graphite substrates were prepared by vacuum evaporation. Bi/W/graphite structure was found to be unsuitable since molten bismuth does not wet tungsten and the bismuth film breaks down into droplets. When Sb/W/graphite was used as a substrate for the deposition of cadmium telluride films by the direct recombination of elements using antimony (or phosphorus) as a dopant, the specimen was heated at 650°C (m.p. of Sb: 630.5°C) after the initial deposition at 500°C to insure the reaction between antimony and cadmium telluride. 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, indicating that the CdTe/substrate interface is rectifying. The use of lead telluride and bismuth telluride as the interlayer was not successful because of their chemical interactions with cadmium telluride.

A series of experiments were carried out to determine the extent of incorporation of antimony into cadmium telluride films. Mullite substrates were used to facilitate the electrical measurements. The partial pressure of cadmium in the reactant mixture was 0.4 Torr, the Cd/Te molar ratio was about 0.9, the substrate temperature was 500^{o}-550^{o}C, and the partial pressure of antimony in the reactant was varied from 5×10^{-4} to 2×10^{-3} Torr. Resistivity measurements were carried out at room temperature using the van der Pauw method. In all cases, the measured dark resistivities were extremely high, and the results were inconsistent. More reproducible results were obtained by carrying out the resistivity measurements under AM1 illumination. The measured resistivity is in the range of $(5\text{-}20) \times 10^{3}$ ohm-cm, as shown in Fig. 13. The resistivity of antimony-doped cadmium telluride films on W/graphite substrates estimated from the forward dark characteristics of Schottky barriers is on the order of 5×10^{3} ohm-cm, which represents the upper limit of the resistivity of cadmium telluride in the thickness directions. Thus, the high lateral resistivity in cadmium telluride films is related to the grain boundary effects.

Schottky barrier type solar cells of 1 cm^{2} area were prepared from antimony-doped cadmium telluride films. The open-circuit voltage was 300-350 mV, and the short-circuit current density was 10-15 mA/cm^{2}; however, the fill factor was only 30-40% due to the non-ohmic CdTe/substrate interface.

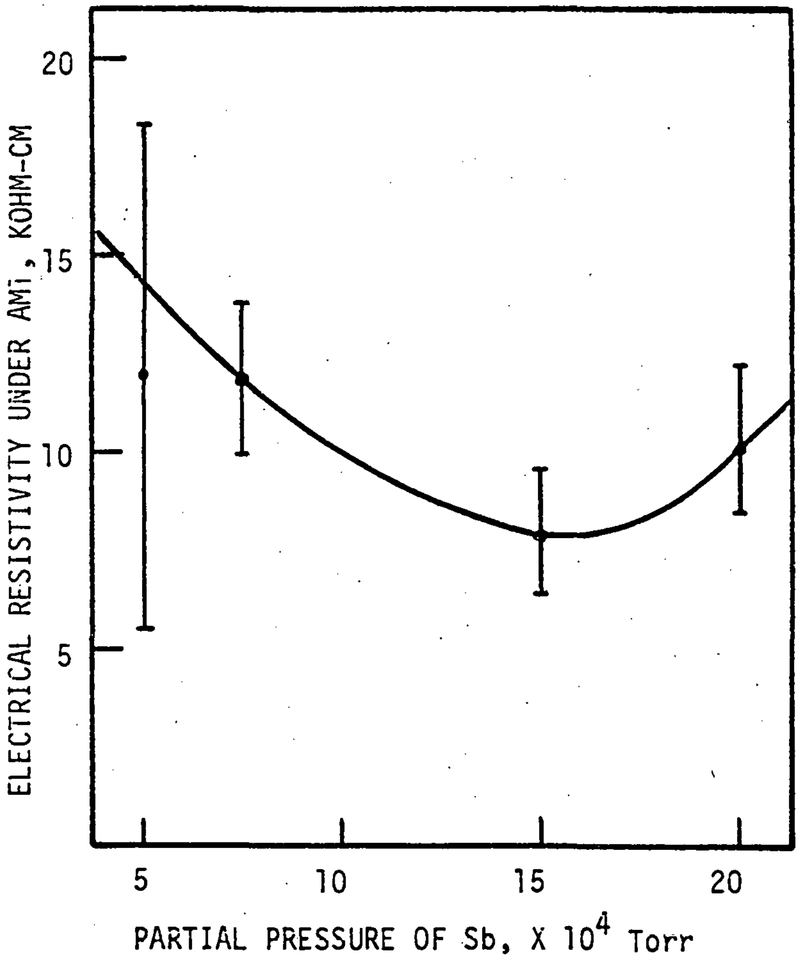


Fig. 13 Lateral resistivity of p-type cadmium telluride films as a function of partial pressure of antimony in the reactant mixture.

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VI. Summary and Recommendations for Future Work

During the course of this program, large grain (>10 μm) cadmium telluride films with minority carrier diffusion length of 0.8-1.8 μm have been prepared by the chemical vapor deposition technique. For photovoltaic devices, however, the deposited films must be pinhole-free, must have controlled resistivity and low CdTe/substrate interface resistance. By using In/W/graphite as substrates for the deposition of n-type films, an ohmic interface is obtained. However, indium diffuses rapidly along the grain boundaries, and low resistivity (10 ohm-cm for example) n-type cadmium telluride films have not been prepared. As a result, solar cells prepared from these films exhibit high dark current, low open-circuit voltage, and low fill factor. Although the short-circuit current is usually higher than 10 mA/cm^2. A number of substrates, such as antimony, bismuth, lead telluride, and bismuth telluride coated graphite, have been used for the deposition of p-type cadmium telluride films; however, all CdTe/substrate interfaces have been found to be rectifying. The use of phosphorus, arsenic, and antimony as dopants have not produced low resistivity p-type films. Solar cells prepared from these films exhibit reasonable short-circuit current densities, up to 15 mA/cm^2; however, the conversion efficiency is relatively low due to high series resistance.

In view of the good microstructure of CVD cadmium telluride films, further work should be directed to (1) the incorporation of n- and p-type dopants to produce low resistivity material, and (2) the search of low cost substrates with low CdTe/substrate interface resistance. It is believed that low resistivity cadmium telluride films can be produced by optimizing the deposition conditions. In parallel to the search of substrates with low interface resistance, back wall cells of the configuration p-CdTe/n-CdS/ITO/glass(substrate) should be investigated.

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