

Thin Film Cadmium Telluride and Zinc Phosphide Solar Cells

A Subcontract Report

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ABSTRACT

This report describes research performed from June 1982 to October 1983 on the deposition of cadmium telluride films by direct combination of the cadmium and tellurium vapor on foreign substrates. Nearly stoichiometric p-type cadmium telluride films and arsenic-doped p-type films have been prepared reproducibly. Major efforts were directed to the deposition and characterization of heterojunction window materials, indium tin oxide, fluorine-doped tin oxide, cadmium oxide, and zinc oxide. A number of heterojunction solar cells were prepared, and the best thin-film IT0/CdTe solar cells had an AM1 efficiency of about 7.2%. Zinc phosphide films were deposited on W/steel substrates by the reaction of zinc and phosphine in a hydrogen flow. Films without intentional doping had an electrical resistivity on the order of 10^6 ohm-cm, and this resistivity may be reduced to about 5×10^4 ohm-cm by adding hydrogen chloride or hydrogen bromide to the reaction mixture. Lower resistivity films were deposited by adding a controlled amount of silver nitrate solution on to the substrate surface. Major efforts were directed to the deposition of low-resistivity zinc selenide in order to prepare ZnSe/ As_3P_2 heterojunction thin-film solar cells. However, zinc selenide films deposited by vacuum evaporation and chemical vapor deposition techniques were all of high resistivity.

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Summary

This is the final Technical Report of a research program "Thin Film Cadmium Telluride and Zinc Phosphide Solar Cells" covering the period June 1, 1982 to October 31, 1983 supported by the Solar Energy Research Institute under Subcontract XL-2-02097-01.

The author regrets to report that considerable inconveniences had to be overcome in order to continue the program during this contract period. The laboratories which had housed the research programs were closed by the University on August 30, 1983, and the Principal Investigator and his associates had to relocate to laboratories 8 miles from the campus. Considerable time was spent in designing and constructing the laboratories, and relocation resulted in personnel turnover, damaged equipment, various operating problems, and considerable delays.

During this reporting period, the deposition of cadmium telluride films by the direct combination of the cadmium and tellurium vapor on foreign substrates has been continued. Nearly stoichiometric p-type cadmium telluride films and arsenic-doped p-type films have been prepared reproducibly. Major efforts were directed to the deposition and characterization of heterojunction window materials, indium tin oxide, fluorine-doped tin oxide, cadmium oxide, and zinc oxide. A number of heterojunction solar cells were prepared, and the best thin film ITO/CdTe solar cells had an AM1 efficiency of about 7.2%.

Zinc phosphide films have been deposited on W/steel substrates by the reaction of zinc and phosphine in a hydrogen flow. Films without intentional doping had an electrical resistivity on the order of 10^6 ohm-cm, and this resistivity may be reduced to about 5×10^4 ohm-cm by adding hydrogen chloride or hydrogen bromide to the reaction mixture. Lower resistivity films were deposited by adding a controlled amount of silver nitrate solution on to the substrate surface. Major efforts were directed to the deposition of low resistivity zinc selenide in order to prepare ZnSe/Zn₃P₂ heterojunction thin film solar cells. However, zinc selenide films deposited by vacuum evaporation and chemical vapor deposition techniques were all of high resistivity. As a result, ITO/ZnSe/Zn₃P₂/W/steel solar cells had V_{oc} of about 0.6 V and I_{sc} of only 2-3 mA/cm². Although ITO/Zn₃P₂/W/steel solar cells has produced I_{sc} of up to 14 mA/cm²; however, the photoresponse degraded rapidly. The formation of thin Zn₃N₂ film on Zn₃P₂ film by ammonia treatment showed no measurable improvements in solar cell characteristics.

I. Introduction

This is the Final Technical Report of a research program "Thin Film Cadmium Telluride and Zinc Phosphide Solar Cells" supported by the Solar Energy Research Institute under Subcontract XL-2-02097-1 during the period June 1, 1982 to October 31, 1983. The major objectives of this contract are (1) to demonstrate CVD grown CdTe devices with a total area greater than 1 cm^2 and photovoltaic efficiencies greater than 8%, and (2) to demonstrate CVD grown Zn_3P_2 devices with a total area greater than 1 cm^2 and photovoltaic efficiencies greater than 5%.

The technical approach used for the cadmium telluride program consists of (1) the deposition and characterization of cadmium telluride films on foreign substrates (such as tungsten coated graphite) with low CdTe/substrate interface resistance by the direct combination of cadmium and tellurium vapor, (2) the control of carrier concentration in p-type cadmium telluride films, and (3) the preparation and characterization of n-ITO/p-CdTe and n-CdS/p-CdTe thin film solar cells. The technical approach used for the zinc phosphide program consists of (1) the deposition and characterization of zinc phosphide films on W/steel substrates, (2) the control of carrier concentration in zinc phosphide films and the reduction of Zn_3P_2 /substrate interface resistance, and (3) the preparation and characterization of n-ZnSe/p- Zn_3P_2 thin film solar cells.

The author regrets to report that considerable inconveniences had to be overcome in order to continue the program during this contract period. The laboratories which had housed the research programs were closed by the University on August 30, 1982 after four days' notice, and the Principal Investigator and his associates had to relocate to laboratories 8 miles

from the campus. Considerable time was spent in designing and constructing the laboratories, and relocating the laboratory furniture and equipment. The closing and relocation resulted in personnel turnover, damaged equipment, various operating problems, and considerable delays.

During this contract period, an improved deposition system for the chemical vapor deposition of cadmium telluride films has been constructed. Major efforts were directed to (1) the deposition of p-type cadmium telluride films, (2) the deposition and characterization of n-type window materials, and (3) the fabrication and evaluation of heterojunction solar cells. Heterojunction solar cells of 1 cm^2 area of the configuration Ta_2O_5 (AR coating) / n-ITO / p-CdTe / Sb / graphite with an AM1 efficiency of about 8% has been produced, thus fulfilling the contract requirement.

The zinc phosphide program has been directed to (1) the deposition and characterization of hydrogen chloride and silver doped zinc phosphide films, (2) the passivation of the surface of zinc phosphide films, (3) the deposition and doping of zinc selenide films, and (4) the preparation and characterization of thin film zinc phosphide heterojunction solar cells. The results thus far do not appear to be promising, and no further work is planned.

The experimental procedures and results on cadmium telluride and zinc phosphide thin films and solar cells are discussed in the following sections.

II. Cadmium Telluride Films and Solar Cells

II.1 Deposition of Cadmium Telluride Films

II. 1. 1 The Deposition Process

The reaction between elemental cadmium and tellurium in a hydrogen flow has been used for the deposition of cadmium telluride films on foreign substrates. This technique has two distinct advantages: (1) a wide range in thickness from a few micrometers to hundreds of micrometers can be achieved and controlled, and (2) the dopant concentration and distribution in the deposit can be controlled by adding an appropriate amount of a dopant into the reaction mixture during the deposition process.

To carry out the deposition of cadmium telluride, a cadmium container, a tellurium container, and the substrate are placed in the appropriate temperature zones of a fused silica reaction tube heated by a multizone furnace. 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_{Cd}^0 and $P_{Te_2}^0$, may be estimated from the temperatures of cadmium and tellurium and the flow rates of hydrogen through the sources and the reaction tube. When $P_{Cd}^0 (P_{Te_2}^0)^{\frac{1}{2}}$ 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

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

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. However, this deduction is not valid since the chemical composition and electrical resistivity of cadmium telluride films have been found to depend strongly on the Cd/Te molar ratio in the reaction mixture.

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:

$$\begin{aligned} n_{\text{CdTe}} &= (P_{\text{Cd}}^0 - P_{\text{Cd}}) V / RT \\ &= (P_{\text{Te}_2}^0 - P_{\text{Te}_2}) V / RT \end{aligned}$$

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.

The partial pressures of cadmium and tellurium in the reaction mixture are determined by the temperatures of the cadmium and tellurium containers and the flow rates of hydrogen through these containers. Since the vapor pressure of the elements vary exponentially with temperature, it is essential to keep the temperature of cadmium and tellurium containers as constant as possible. During this reporting period, an improved deposition system for cadmium telluride films has been constructed. It consists of an eight-zone furnace with each zone separately heated and independently controlled. This multizone furnace is capable of maintaining the temperatures of cadmium and tellurium containers within $\pm 1^\circ\text{C}$. Further, the

cadmium and tellurium containers have appreciable heat capacity, thus further minimizing the effects of temperature fluctuations. Also, mass flow controllers manufactured by the Tylan Corporation (Carson, California) were used to control the flow of hydrogen through the cadmium and tellurium containers. However, the mass flow controllers are not fool-proof, and conventional rotameters were used in series with the mass flow controllers for routine checks.

II.1.2. Substrates

The selection of substrates for the deposition of cadmium telluride films requires careful considerations. Because of the chemical environment in the deposition of cadmium telluride films and the use of relatively high temperatures, 500°-600°C, the choice of substrates is rather limited. Graphite appears to be a suitable substrate for large area front wall solar cells. Several types of graphite, such as grade DFP-2 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, $5.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. 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 $1.65\text{-}1.75\text{g/cm}^{-3}$ (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 may be difficult to achieve. In many cases, a thin layer of an impervious material, such as carbon, silicon, or tungsten, was deposited on graphite substrates to provide a homogeneous surface.

In addition to coated graphite, alumina was also used as a substrate to facilitate the characterization of electrical properties of cadmium telluride films.

POCO DFP-2 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 at 1100°C, the thermal reduction of trichlorosilane at 1150°C, and the thermal reduction of tungsten hexafluoride at 550°C. The graphite substrates were supported on a graphite susceptor in a fused silica reaction tube, 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.

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 $\exp(-C\phi^{\frac{1}{2}}t)$, 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 $n^+-\text{CdTe}$ is similar to the electron affinity, while that of lightly doped $n\text{-CdTe}$ 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 deposited on W/graphite by evaporation were found to form low-resistance ohmic contacts to n-type cadmium telluride films.

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. A number of dopants were used at the p-CdTe/substrate interface. For example, antimony, bismuth or their alloy was deposited on W/graphite by vacuum evaporation; the dissolution of antimony or bismuth in cadmium telluride may 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 graphite by evaporation. Also, a thin film of gold or gold-antimony eutectic (m.p. 500°C) was also deposited on graphite substrate.

II.1.3. Effects of Process Parameters

The problems associated with the preparation of front-wall large area thin film cadmium telluride heterojunction solar cells are well recognized: (1) the difficulty of depositing low resistivity p-type

cadmium telluride films reproducibly, (2) the formation of low resistance contact of p-CdTe film to the substrate, and (3) the deposition of large area pinhole-free CdTe films.

The possibility of eliminating pinholes in large area films by varying the substrate temperature and partial pressures of cadmium and tellurium in the reaction mixture was investigated. Since the nucleation rate increases with decreasing substrate temperature, a series of experiments were carried out to deposit cadmium telluride films at 450°C, instead of 550°C used in this program during the past three years, using partial pressures of cadmium in the range of 0.1-0.25 Torr. The deposition rate of cadmium telluride was found to be very low in all cases, less than 4 $\mu\text{m/hr}$, due to the low supersaturation of cadmium telluride at the substrate surface (K_{CdTe} is $1.2 \times 10^{-11} \text{ atm}^2$ at 450°C as compared with $4.3 \times 10^{-8} \text{ atm}^2$ at 550°C). The deposition rate of cadmium telluride at 500°C, 7-8 $\mu\text{m/hr}$, was also too low to be useful for the deposition process. It is concluded that substrate temperatures of 550°C or higher must be used to obtain reasonable deposition rates.

The deposition of p-CdTe films was carried out by using arsine as a dopant. To facilitate the electrical characterization of these films, alumina was used as a substrate, and the van der Paul technique was used for the measurement of carrier concentration and electrical resistivity. Since the measurement was made in the direction parallel to the substrate surface, the potential barriers at grain boundaries could dominate the electrical resistivity. The resistivity versus As/Cd or As/Te plot always exhibited a minimum, although the magnitudes of the dopant ratio and the minimum resistivity could vary considerably from one series of

experiments to another. The current work is concerned with the measurement of electrical resistivity in the thickness direction of the film since this resistivity is more relevant to the operation of devices.

Considerable efforts were directed to the reduction of p-CdTe/substrate interface resistance. The technical approach consisted of (1) the deposition of a thin film of potentially useful material on graphite substrate, (2) the deposition of a p-CdTe film on the coated substrate, (3) the formation of a gold ohmic contact on the surface of CdTe by evaporation and heat treatment, and (4) the measurement of dark current-voltage characteristics of the resulting structure. A linear relation would be obtained if the p-CdTe/substrate interface is of low resistance. However, it was difficult to arrive at definitive conclusions since the p-CdTe/substrate interface resistance depends on the resistivity of CdTe and the results are not always reproducible. The contact materials investigated may be classified into three types: (1) p-type tellurides such as Bi_2Te_3 and PbTe , (2) p^+ -semiconductors, such as gallium arsenide and silicon, and (3) p-type dopant for CdTe including Au, Cu, Bi, Sb, Au-Sb eutectic. Bismuth telluride and lead telluride were prepared by the direct synthesis of stoichiometric quantities of the elements in a fused silica tube and were deposited on the surface of graphite substrates by vacuum evaporation. Both Bi_2Te_3 and PbTe were found to react with cadmium telluride. P^+ -GaAs deposited on the surface of graphite substrates by the halide process was also found to react with cadmium telluride. P^+ -Si deposited on graphite substrates by the thermal reduction of trichlorosilane is inert toward p-CdTe. The p-CdTe/ p^+ -Si interface resistance is considerably less than that of p-CdTe/W, but is higher than that of p-CdTe/graphite.

Among p-type dopants for cadmium telluride, gold and copper were found to diffuse rapidly into cadmium telluride films. For example, gold could not be detected at the interface after a Au (500Å)/graphite substrate was used for the deposition of CdTe films at 550°C. The use of Sb/graphite substrates has produced films with low interface resistance (less than 2 ohm-cm²) in many cases; however, the results have not been reproducible due presumably to the varying resistivity of p-CdTe films.

II. 2. Deposition and Characterization of Window Materials

Cadmium telluride thin films are not suitable for homojunction solar cells mainly because the difficulties associated with the formation of a very shallow junction and the formation of a high conductivity surface layer. The heterojunction structure requires a large band-gap semiconductor with high optical transmission in the visible region and high electrical conductivity. The commonly used high conductivity window materials are non-stoichiometric or doped large band-gap oxide or sulfide. The oxides of cadmium (CdO, $E_g=2.2$ eV), zinc (ZnO, $E_g=3.3$ eV) indium (In_2O_3 , $E_g=3.7$ eV), and their solid solutions are all suitable. Major efforts during this reporting period have been directed to the deposition and characterization of these films. The techniques used for the deposition of transparent semiconductor films included ion beam sputtering, chemical vapor deposition, and spray pyrolysis. Each technique has its own merits. For example, high conductivity transparent oxide films can be deposited on substrates at essentially room temperature by ion-beam sputtering; however, the deposition rate is very low, and the substrate may suffer mechanical damages by the charged particle bombardment. The chemical vapor deposition technique has the advantage of depositing films of controlled

composition at high rates while the spraying technique is simple and economical. Both techniques require relatively high substrate temperatures, 300°C or higher, and further work should be directed to the use of lower substrate temperatures. For example, the substrate temperature may be reduced by using the plasma-enhanced chemical vapor deposition techniques or by using a lower rate in the spray pyrolysis technique. The current results on the deposition of tin-doped indium oxide (ITO), fluorine-doped tin oxide ($\text{SnO}_2\text{:F}$), cadmium oxide (CdO), and zinc oxide (ZnO) are summarized below.

II.2.1. Tin doped Indium Oxide (ITO)

Indium oxide films are widely used as transparent conductors and are polycrystalline (typical grain size: 100 Å) with a cubic structure ($a=10.118$ Å). They exhibit a direct optical band gap of 3.55 to 3.75 eV. Good quality indium oxide films have been reported to have mobilities of $10\text{--}75\text{ cm}^2/\text{V}\cdot\text{sec}$, carrier concentrations of $10^{19}\text{--}10^{20}\text{ cm}^{-3}$, and electrical resistivities on the order of $10^{-3}\text{ ohm}\cdot\text{cm}$. The carrier concentration in indium oxide films may be further increased by using tin oxide as a dopant. Tin-doped indium oxide (ITO) films containing 5-10% tin oxide retain the bulk structure of indium oxide with a slight increase in the lattice parameter ($10.188\text{ Å} < a < 10.31\text{ Å}$). ITO films with grain sizes of 400-600 Å may show a preferred $\langle 100 \rangle$ or $\langle 111 \rangle$ orientation depending on the deposition conditions; however, the electrical and optical properties are independent of the orientation effects. Films with carrier concentration of 10^{21} cm^{-3} and resistivity of 7×10^{-5} to $5 \times 10^{-4}\text{ ohm}\cdot\text{cm}$ have been reported.

ITO films have been deposited by various techniques such as evaporation, sputtering, chemical vapor deposition, and spray pyrolysis. In this work, ITO films were deposited by ion-beam sputtering using a Commonwealth Scientific Corporation (Alexandria, Virginia) Millatron IV coater with a cryogenic pumping system. Briefly, an accelerated argon ion beam is directed to the surface of a 5" diameter water-cooled ITO target, supplied by the Materials Research Corporation (Orangesburg, New York). The decelerating ions eject molecules from the target material, and these molecules are deposited onto the substrate. The rate of deposition may be controlled by controlling the energy of the incident ion beam. Further, the beam energy is dissipated in the target, and the substrate remains essentially at room temperature. Prior to the deposition process, the surface of the substrate and the target may be cleaned in the ion beam.

The important process parameters in the deposition of ITO films by ion beam sputtering include the accelerating voltage and current of the argon ion beam, the partial pressure of oxygen in the deposition chamber, and the separation between the target and the substrate (glass slides were used as substrates to facilitate the electrical and optical measurements). To simplify the investigation of the effects of process parameters, the distance between target and the substrate was fixed at 10 cm, and the argon ion was accelerated at 1 kV with a beam current of 50 mA, as suggested by the manufacturer. To carry out the deposition process, the chamber was evacuated to a pressure of 10^{-6} Torr, and an argon flow through the chamber was adjusted to maintain a pressure of 4×10^{-4} Torr.

The oxygen partial pressure in the deposition chamber was controlled in the range of $(0-14) \times 10^{-5}$ Torr by using a needle valve. Prior to the deposition of ITO films on the substrate, the target was sputtered for 10-15 minutes followed by deposition for 30-60 minutes.

The deposited films were evaluated by thickness (Sloan Dektak), electrical resistivity (four-point probe and van der Pauw techniques), carrier mobility (the van der Pauw technique), and optical transmission (Cary 17 spectrophotometer) measurements. The deposition rate of ITO films, about 100 Å/min, varies slightly with the partial pressure of oxygen. The electrical resistivity of ITO films depends strongly on the partial pressure of oxygen during the deposition process. Figure 1 shows the resistivity of ITO films on glass slides, as measured by the four-point probe technique, as a function of the oxygen partial pressure (the resistivities measured by the van der Pauw technique were in good agreement with those by the four-point probe technique). Without using oxygen in the plasma, the resistivity was 2.5×10^{-2} ohm-cm. The resistivity of ITO films decreases rapidly with increasing oxygen concentration, and the minimum resistivity is about 6×10^{-4} ohm-cm obtained at an oxygen partial pressure of 6×10^{-5} Torr.

The use of thermoelectric probe indicated that some regions of the low resistivity ($< 10^{-3}$ ohm-cm) ITO films were of p-type conductivity. However, all films were of n-type conductivity from Hall measurements. It is possible that local inhomogeneities exist where indium behaved as an acceptor in tin oxide. Figure 2 shows the room temperature carrier concentration and Hall mobility in ITO films as a function of the oxygen partial pressure during deposition. The electron mobility is in the range

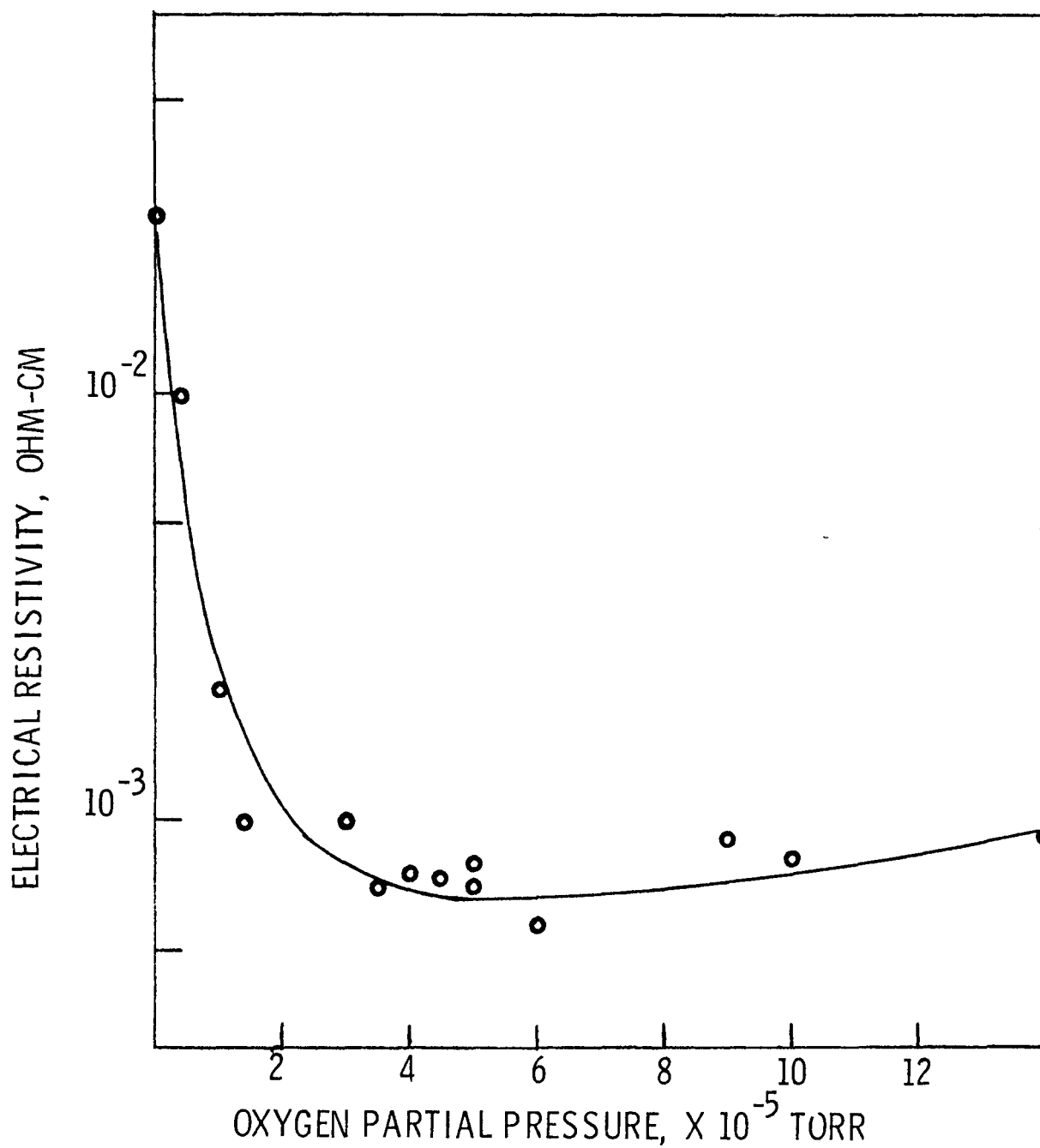


Fig. 1 The electrical resistivity of ion-beam sputtered indium tin oxide films as a function of the oxygen partial pressure during the deposition process.

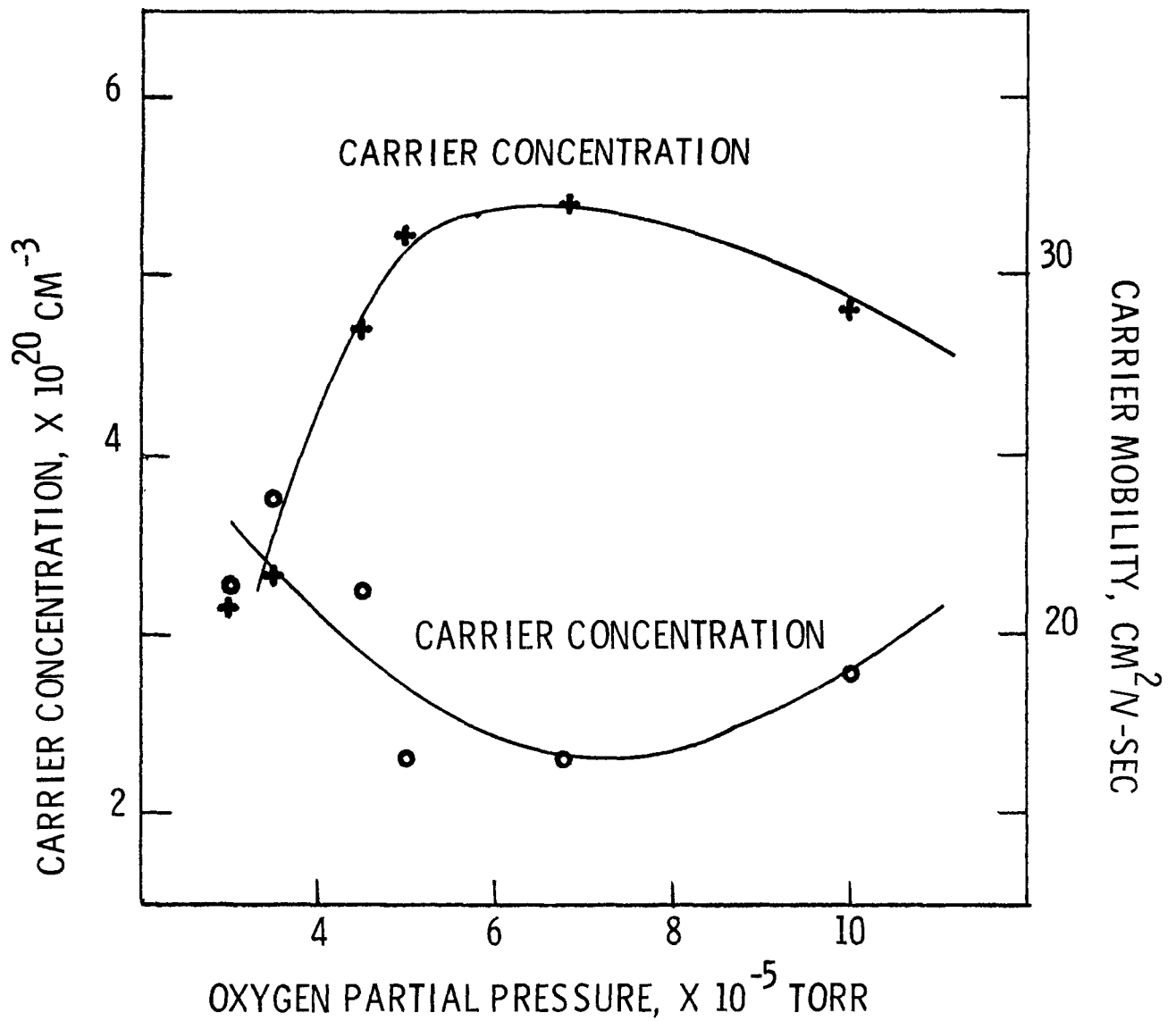


Fig. 2 The room temperature carrier concentration and Hall mobility in ITO films a function of the oxygen partial pressure.

of $20\text{--}30\text{ cm}^2/\text{V-sec}$, with a maximum of about $30\text{ cm}^2/\text{V-sec}$. in films deposited at oxygen partial pressure of $(6\text{--}8) \times 10^{-5}$ Torr. Figure 3 shows the electrical resistivity, carrier concentration, and Hall mobility of an ITO film as a function of temperature in the range of $20^\circ\text{--}200^\circ\text{C}$. As the temperature is increased from the room temperature, the mobility decreased and the carrier concentration increased. In the temperature range $60^\circ\text{--}160^\circ\text{C}$, the properties of the ITO film are essentially temperature independent.

The optical transmission of ITO films, 80-85% in the wavelength range 450-800 nm, is essentially independent of oxygen partial pressure at pressures higher than about 3×10^{-5} Torr.

II. 2.2. Fluorine-Doped Tin Oxide ($\text{SnO}_2\text{:F}$)

Tin oxide (SnO_2) is the first transparent conductor received significant commercial applications. Many papers on the preparation and properties of SnO_2 films have been published. Pure SnO_2 films exhibit a direct optical band gap of 3.9-4.3 eV. Undoped SnO_2 films are generally polycrystalline with grain sizes of 200-300 Å and retain the tetragonal rutile structure. The n-type conductivity of undoped SnO_2 films is due primarily to its non-stoichiometry, typically with a carrier concentration of $10^{19}\text{--}10^{20}\text{ cm}^{-3}$ and a resistivity of 10^{-3} to 10^{-2} ohm-cm. Dopants, such as antimony or fluorine, is incorporated substitutionally. Fluorine-doped SnO_2 ($\text{SnO}_2\text{:F}$) films are polycrystalline and retain the rutile structure with no change in lattice parameter.

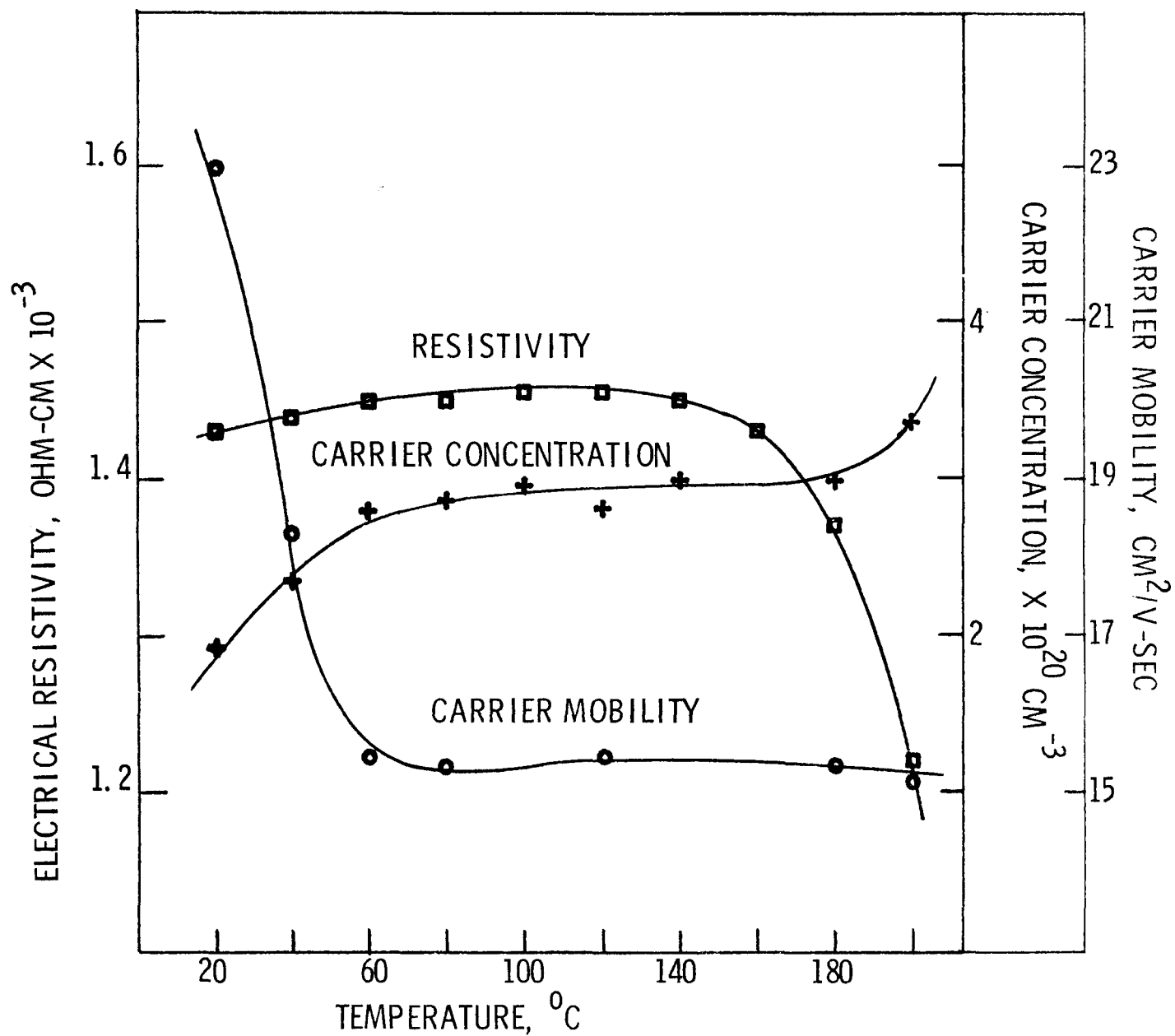


Fig. 3 The electrical resistivity, carrier concentration, and Hall mobility in an ITO film as a function of temperature.

In this work, $\text{SnO}_2\text{:F}$ films have been deposited by CVD using the oxidation of tetramethyltin in a helium atmosphere containing trifluorobromomethane (Freon 13B1) as the dopant. Tetramethyltin is a convenient source material since it is stable in air and has a vapor pressure of about 100 Torr at 23°C. The deposition process was carried out in a horizontal fused silica reaction tube of 55 mm I.D. The substrates, Corning 7059 glass, were supported on a silicon carbide-coated graphite in the reaction tube, and the susceptor was heated externally with an rf generator. A thermal couple inserted into the susceptor was used to monitor the substrate temperature. A series of experiments were carried to determine the optimum process parameters. The typical flow rates used for the deposition of undoped SnO_2 films are: $\text{He}=15 \text{ l/min}$, $\text{O}_2=400 \text{ cc/min}$, and $\text{He thru } (\text{CH}_3)_4\text{Sn at } 25^\circ\text{C}=120 \text{ cc/min}$ (the partial pressure of $(\text{CH}_3)_4\text{Sn}$ in the reaction mixture is approximately 0.7 Torr). The deposition rate of SnO_2 at 450°C is approximately 350 \AA/min as measured by the Sloan Dektak profilometer, and the resistivity of the film, measured by the four-point probe technique, is 20-25 ohm-cm. By adding 20 cc/min of trifluorobromomethane to the reaction mixture, the resistivity of the film may be reduced to about 10^{-4} ohm-cm. The $\text{SnO}_2\text{:F}$ films are highly transparent in the visible region; Figure 4 shows the optical transmission of a $0.6 \text{ }\mu\text{m}$ thick film in the wavelength range 400-800 nm.

II.2.3. Cadmium Oxide (CdO) Films

Cadmium oxide (CdO) with a reported energy gap of 2.2-2.6 eV at room temperature is suitable as a window material for heterojunction devices. Thin films of CdO has not been extensively investigated. In

OPTICAL TRANSMISSION

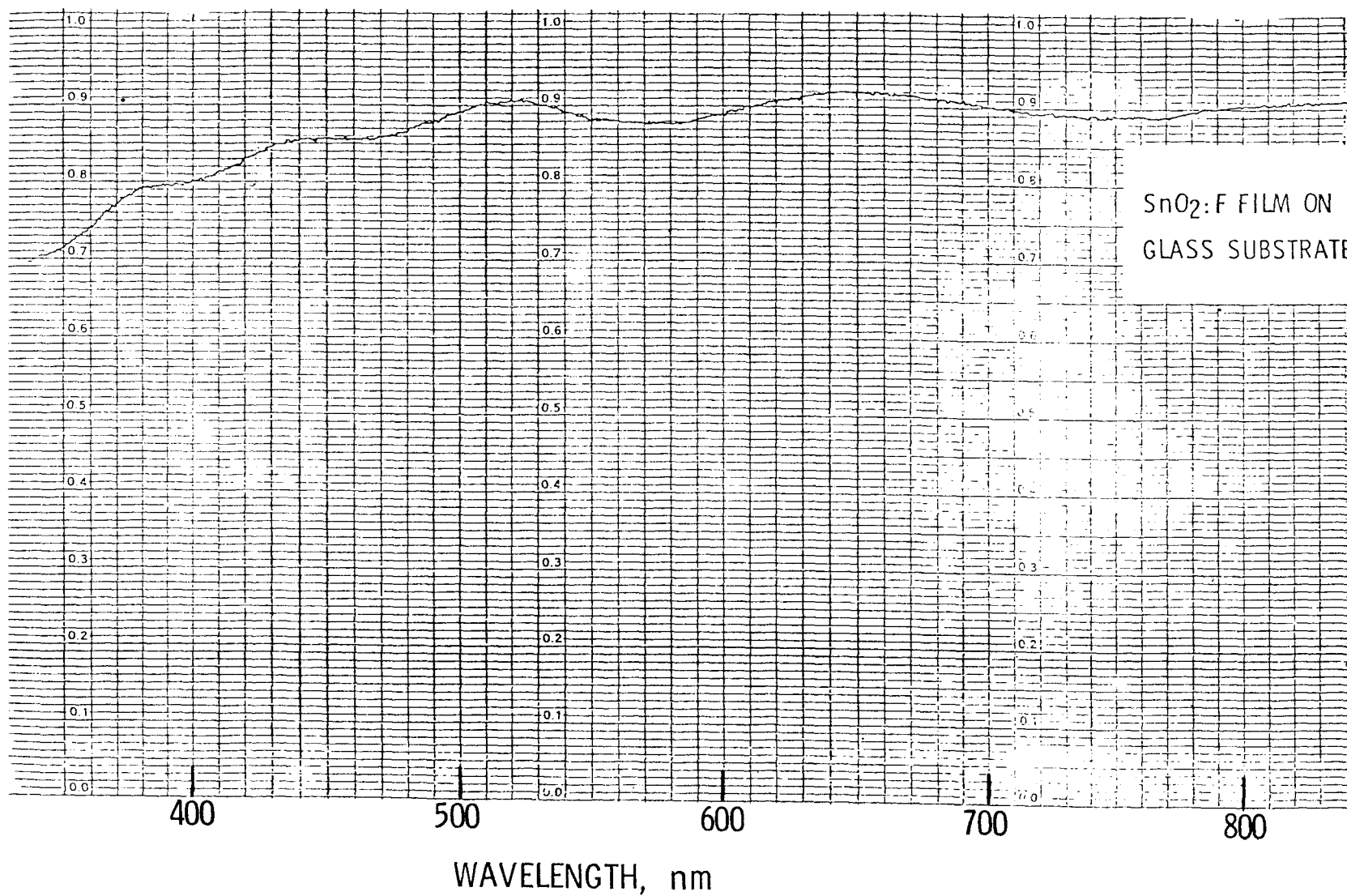


Fig. 4 The optical transmission of a $\text{SnO}_2\text{:F}$ film of about $0.6 \mu\text{m}$ thickness in the wavelength range 400-800 nm.

this work, the ion-beam sputtering of a hot-pressed CdO target, supplied by the Materials Research Corporation, was used for the deposition of CdO films on glass substrates. Similar to the deposition of ITO films by ion-beam sputtering, the distance between the target and the substrate was fixed at 10 cm, the argon-ion was accelerated at 1 kV with a beam current of 50 mA. The deposition chamber was evacuated to 10^{-6} Torr or less, argon flow was adjusted to maintain a pressure of 4×10^{-4} Torr in the chamber, and the plasma was initiated. Under these conditions, the partial pressure of oxygen in the plasma is the most important process parameter determining the properties of cadmium oxide films. The lowest electrical resistivity, measured by the four-point probe technique, was 2×10^{-3} ohm-cm obtained under an oxygen partial pressure of 2×10^{-5} Torr. The electron mobility of this film measured by the van der Paul technique was approximately $10 \text{ cm}^2/\text{V-sec}$, corresponding to a carrier concentration of $3 \times 10^{20} \text{ cm}^{-3}$. The deposition rate of CdO films is approximately $0.3 \text{ } \mu\text{m/hr}$, essentially independent of the oxygen partial pressure. Figure 5 shows the optical transmission of a CdO films of $0.3 \text{ } \mu\text{m}$ thickness in the wavelength range 400-800 nm. The relative high transmission at 500 nm indicates that the energy gap of CdO is appreciably higher than 2.4 eV.

II. 2.4. Zinc Oxide (ZnO) Films

Zinc oxide (ZnO) is technologically important because of its large electromechanical coupling coefficients. It crystallizes in the Wurtzite structure, and zinc oxide films retain the bulk Wurtzite structure. Several techniques, such as sputtering, CVD, and spray pyrolysis, have been used for the deposition of ZnO films. Better quality films have resistivities in the range of 6×10^{-4} to 10^{-3} ohm-cm, carrier mobilities

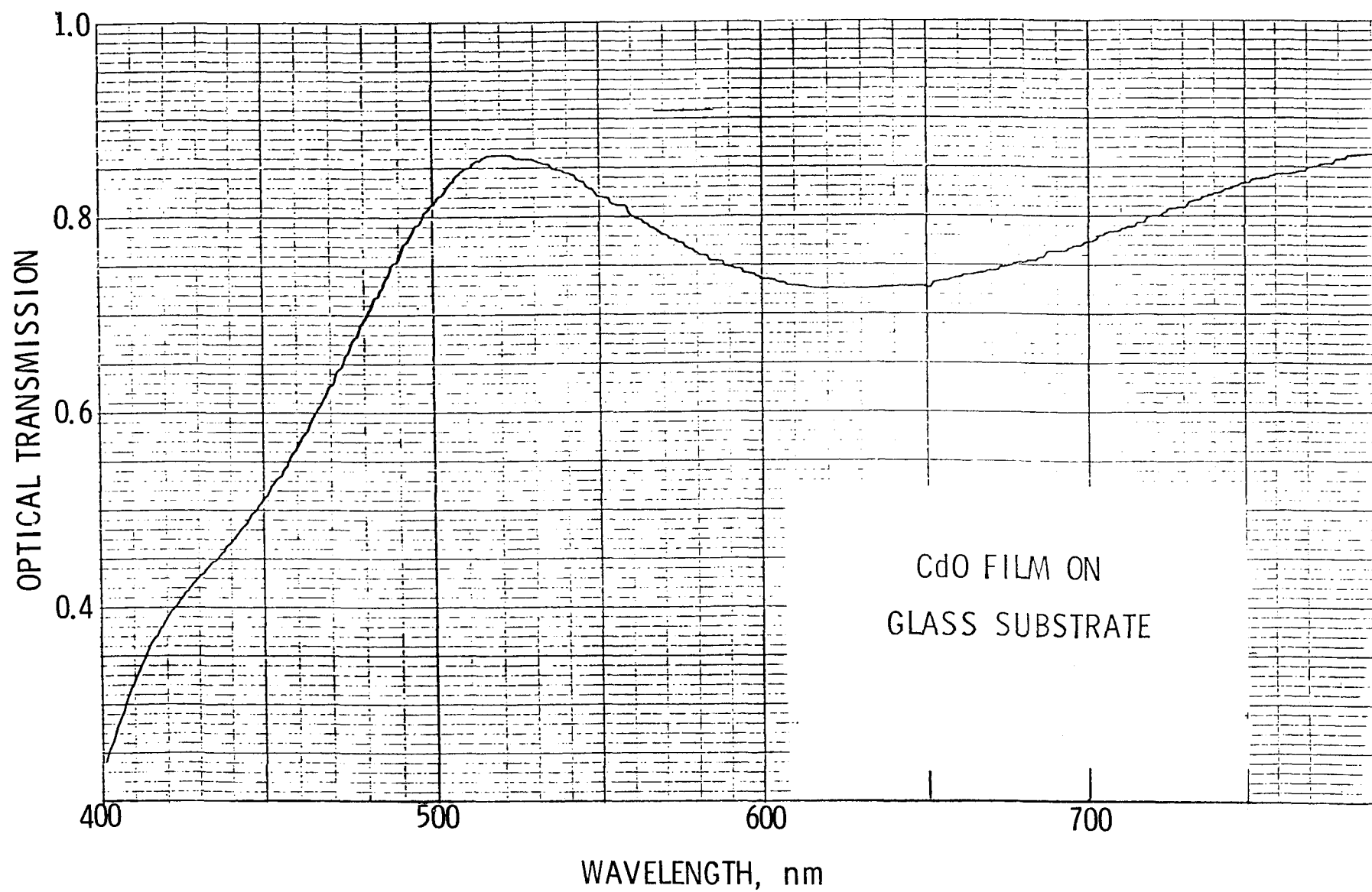


Fig. 5 The optical transmission of a CdO film of about $0.3 \mu\text{m}$ thickness in the wavelength range 400-800 nm.

of 20-30 $\text{cm}^2/\text{V-sec}$, and optical transmission in excess of 90% in the visible region.

Ion-beam sputtering was also used for the deposition of ZnO films on glass substrates under conditions similar to those for the deposition of ITO and CdO films. A hot pressed zinc oxide disc of 5 cm diameter, purchased from the Materials Research Corporation, was used as the target. The electrical resistivity of ZnO films was also found to depend strongly on the partial pressure of oxygen during the deposition process. Figure 6 shows the room temperature electrical resistivity of zinc oxide films as a function of the oxygen partial pressure. Without oxygen, the resistivity was about 0.08 ohm-cm, and the minimum resistivity obtainable was about 0.03 ohm-cm, considerably higher than that reported in the literature. This is due partly to the poor carrier mobility in the ion beam sputtered zinc oxide films, 2-3 $\text{cm}^2/\text{V-sec}$ (Fig. 7) as compared with 20-30 $\text{cm}^2/\text{V-sec}$ in better quality films. The carrier concentration in ion-beam sputtered ZnO films is about $10^{20}/\text{cm}^3$, essentially independent of temperature, as shown in Fig. 7.

II.2.5. Conclusions

Considerable efforts have been devoted to the deposition of high conductivity, transparent oxide films as window materials for heterojunction solar cells: ion-beam sputtering for ITO, CdO, and ZnO, and CVD for $\text{SnO}_2:\text{F}$. The properties of ITO and $\text{SnO}_2:\text{F}$ films are very similar to those reported in the literature, while very little is known concerning the properties of CdO films. However, ion-beam sputtering is a slow and expensive process, and CVD requires relatively high substrate temperatures.

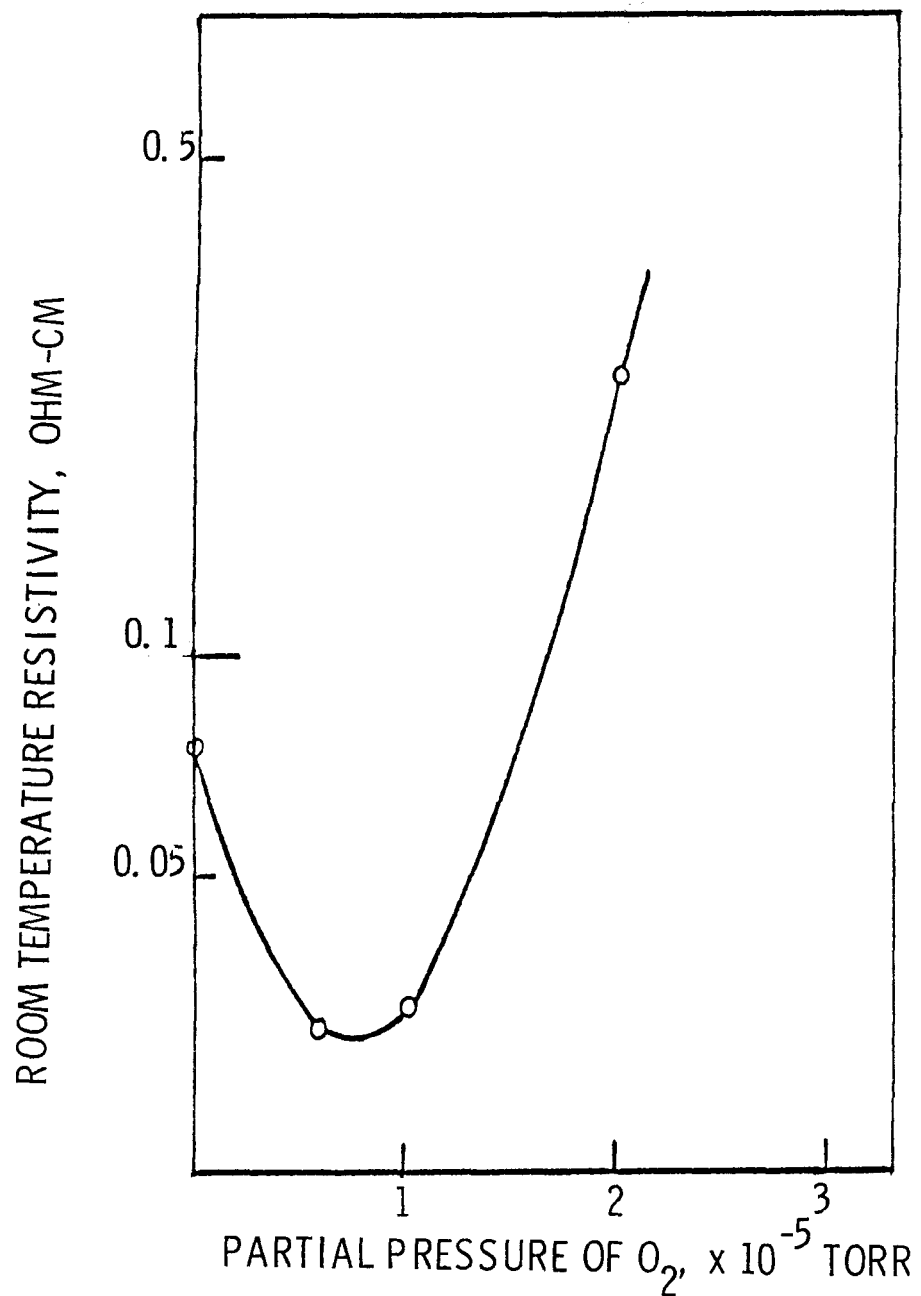


Fig. 6 The electrical resistivity of ion-beam sputtered zinc oxide films as a function of the oxygen partial pressure during the deposition process.

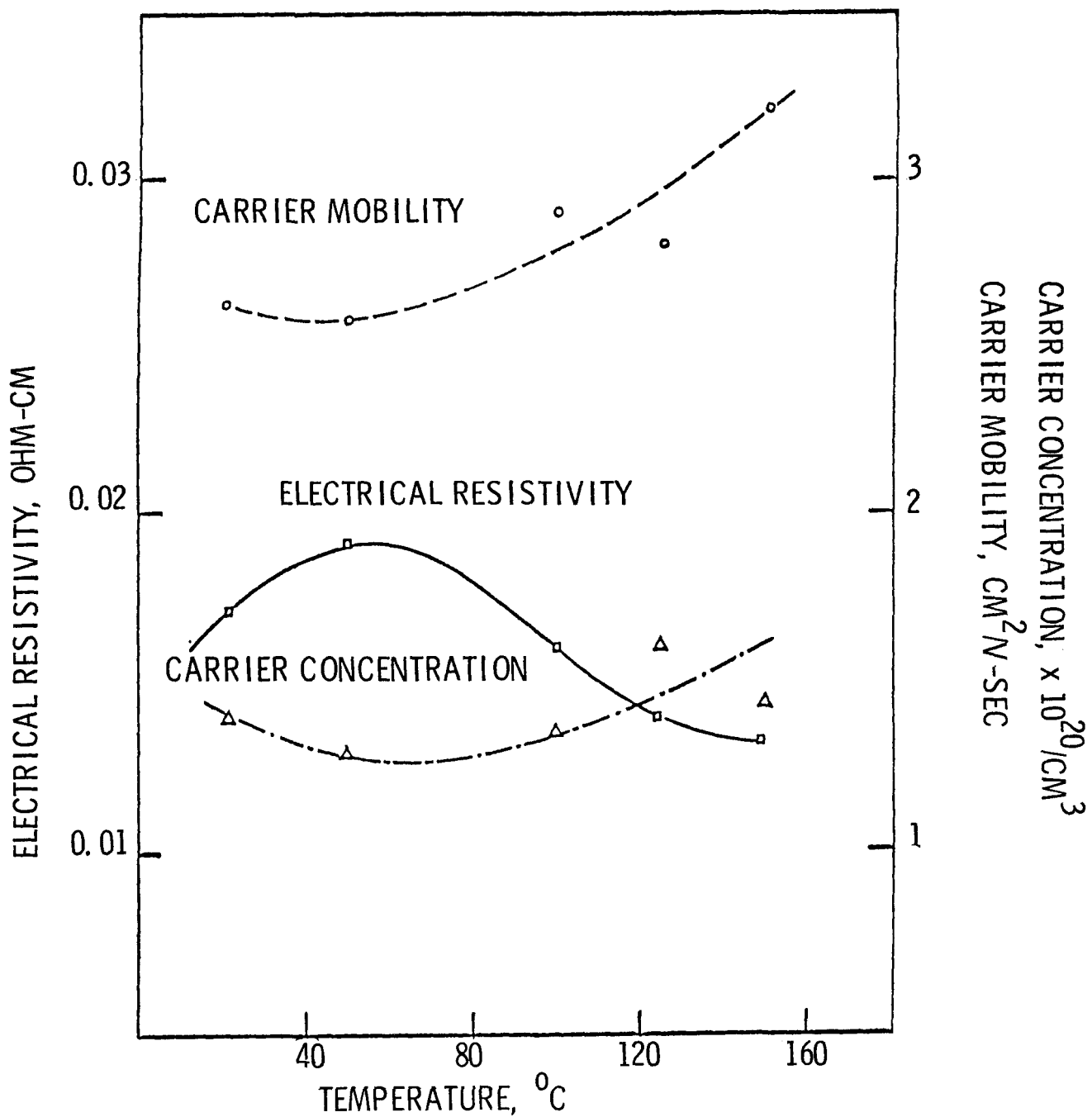


Fig. 7 The electrical resistivity, carrier concentration, and Hall mobility in a zinc oxide film as a function of temperature.

Further work should be directed to overcome these problems. For example, plasma-assisted CVD and spray pyrolysis have considerable promise and will be investigated in detail.

II.3. Thin Film Solar Cells

Many thin film cadmium telluride heterojunction solar cells were prepared from p-CdTe/Sb/W/graphite structures, where the CdTe film consisted of two regions: (1) 10-15 μm of As-doped CdTe of about 200 ohm-cm resistivity to minimize the CdTe/substrate interface resistance and to eliminate pinholes in the film, and (2) 2-3 μm of undoped, nearly stoichiometric, p-type CdTe to provide better minority carrier diffusion length. Ion-beam sputtered ITO films were used as the heterojunction partners in most cases, and ion-beam sputtered CdO film and CVD $\text{SnO}_2\text{:F}$ films were used in a few experiments. The $\text{SnO}_2\text{:F/CdTe}$ solar cells exhibited very poor photoresponse due presumably to the high temperature used in the chemical vapor deposition of $\text{SnO}_2\text{:F}$ films.

The ITO/CdTe solar cells were prepared by the ion-beam sputtering of indium tin oxide in an oxygen partial pressure of 6×10^{-5} Torr onto the surface of CdTe film for 1 hour (thickness of ITO=0.5 to 0.6 μm). The grid contact, 10 lines per cm, was formed by the evaporation of aluminum or silver through a metal mask. An antireflection (and protective) coating of tantalum pentoxide was also deposited by ion-beam sputtering. The current-voltage characteristics of the solar cells were measured under illumination with G.E. ELH quartz-halogen lamps equivalent to AM1 conditions. The open-circuit voltage was up to 0.7 V, and the short-circuit current density was up to 20 mA/cm^2 . However, the fill factor

varies widely, 30-65%, due to the poor reproducibility of the CdTe/substrate interface resistance. The best cell has an AM1 efficiency of about 7.2%; an example of the illuminated current-voltage characteristics is shown in Figure 8, and the quantum efficiency of this cell is given in Figure 9.

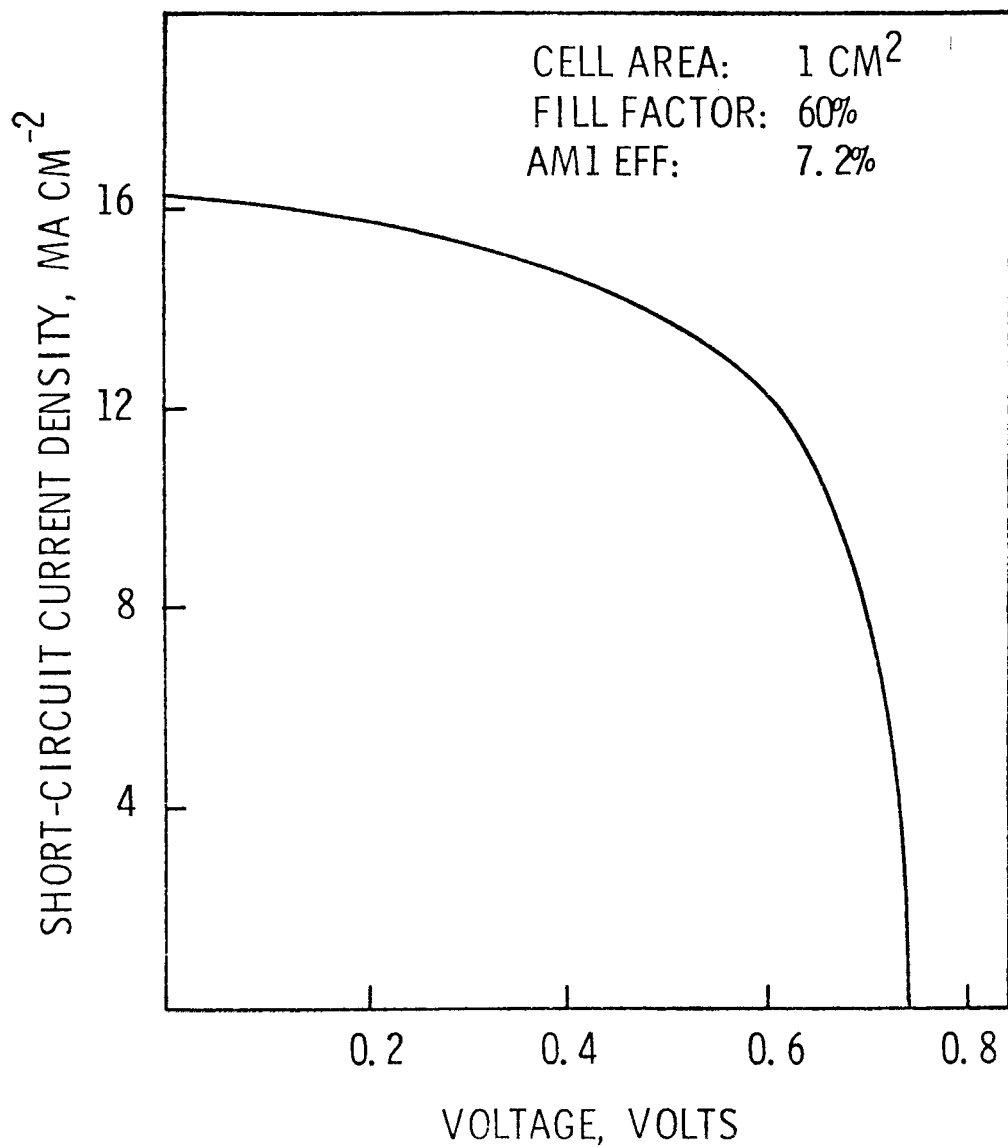


Fig. 8 Illuminated current-voltage characteristics of a Ta₂O₅/ITO/p-CdTe/Sb/W/graphite solar cell under simulated AM1 conditions.

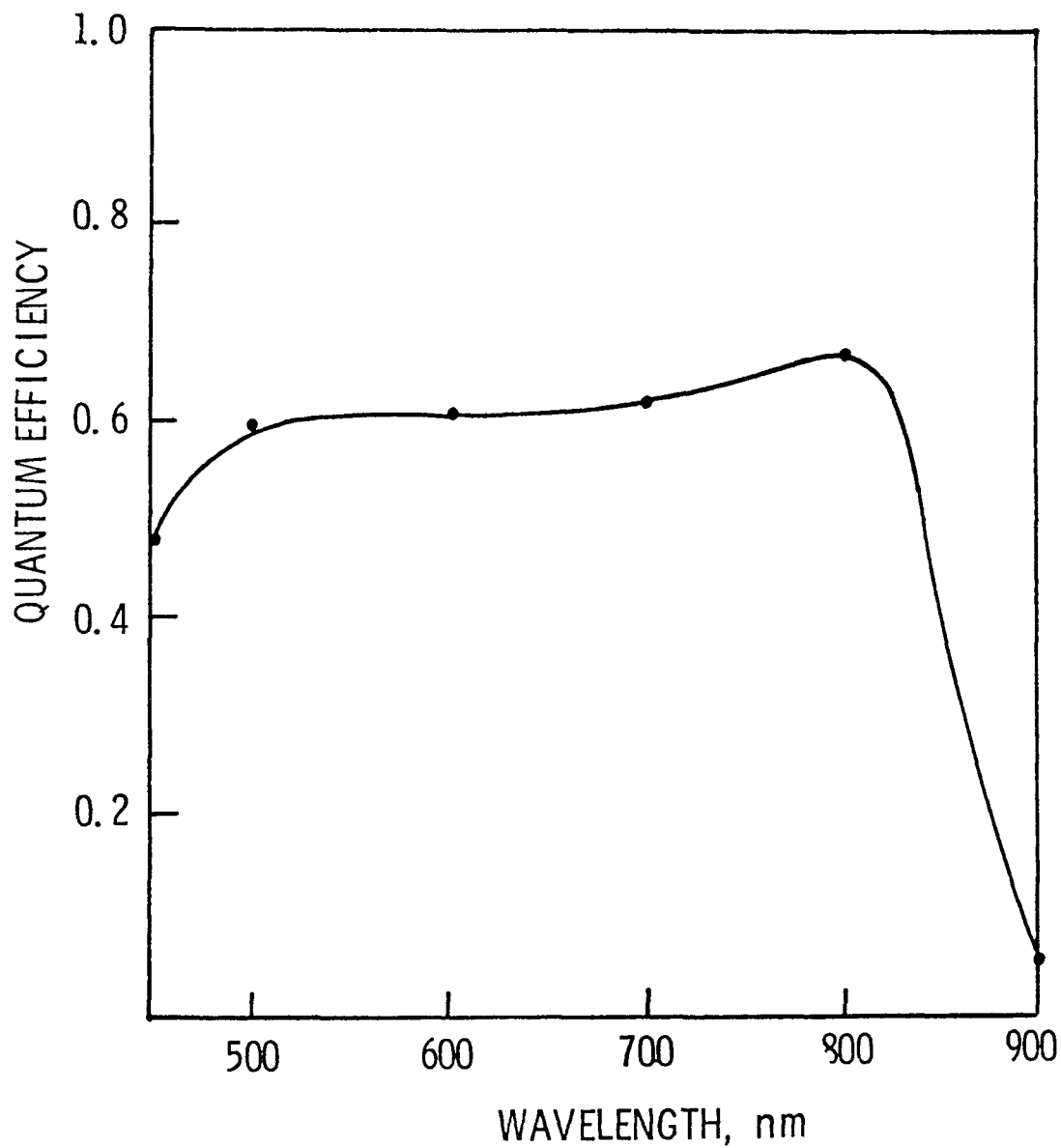


Fig. 9 Quantum efficiency of the solar cell shown in Figure 8.

III. Zinc Phosphide Films and Solar Cells

III. 1. Deposition and Properties of Zn₃P₂ Films

The deposition of zinc phosphide films on foreign substrates has been carried out by the reaction between zinc and phosphine in a gas flow system. A zinc container (carbon-coated fused silica) was placed in an appropriate temperature zone (about 650°C) of a fused silica reaction tube of 55 mm ID, and hydrogen was used to carry zinc vapor to the surface of the substrate. A hydrogen-phosphine mixture containing about 15% phosphine was also introduced to the substrate surface where the heterogeneous reaction occurs to deposit zinc phosphide. Because of the large linear thermal expansion coefficient of zinc phosphide, $(14 \pm 1) \times 10^6 \text{ } ^\circ\text{C}^{-1}$, the choice of substrates is rather limited. Several types of steel, such as U.S. Steel Vitraenamel I, a low carbon steel with a linear thermal expansion coefficient of $14 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ in the temperature range 25°-700°C, was used. This material is widely used for porcelain enameling applications and is available in sheet form of 0.6-1.5 mm in thickness.

Because of the high diffusion rate of iron in zinc phosphide, a diffusion barrier must be used. The diffusion barrier should be chemically inert toward zinc phosphide and steel at high temperatures and should form low resistance ohmic contact with zinc phosphide. The use of carbon and tungsten as diffusion barriers was investigated. Carbon deposited by the pyrolysis of propane in an inert atmosphere was not adherent to steel. Tungsten deposited by the thermal reduction of tungsten hexafluoride with hydrogen did not form a low resistance contact with high resistivity zinc phosphide. The contact resistance was significantly reduced when zinc phosphide was doped with acceptors of a concentration of 10^{16} cm^{-3} or higher.

The composition of deposited Zn_3P_2 films depends on the PH_3/Zn molar ratio in the reaction mixture, the temperatures of the reaction zone and the substrate. It has been demonstrated previously that elemental phosphorus is required for the formation of zinc phosphide and that nearly complete dissociation of phosphine is essential for the efficient utilization of phosphine. While phosphine is thermochemically unstable at room temperature, its dissociation in a flow system requires relatively high temperatures, $800^\circ\text{--}900^\circ\text{C}$. The substrate temperature and the composition and flow rate of the reactant mixture are important factors affecting the deposition rate and properties of zinc phosphide. Zinc phosphide films deposited on steel and tungsten-coated steel substrates are tightly adherent to the substrate. Nearly stoichiometric Zn_3P_2 films were deposited at a PH_3/Zn molar ratio of 10 or higher; however, slight deviation of Zn_3P_2 films from stoichiometry does not degrade its photovoltaic characteristics. The microstructure of Zn_3P_2 films depends strongly on the substrate temperature. The film deposited at $550^\circ\text{--}600^\circ\text{C}$ consists of relatively large grains with well-developed faces as compared with that deposited at 500°C . At higher substrate temperatures, 700°C , for example, the grain size also decreases due presumably to the dissociation of zinc phosphide. Thus, most of the deposition experiments were carried out at $500^\circ\text{--}575^\circ\text{C}$. Zn_3P_2 films deposited on W/steel substrates without intentional doping were always p-type with high electrical resistivity, about 10^6 ohm-cm. The hole mobility estimated from the van der Pauw measurements on Zn_3P_2 films on insulating substrates was $(2\text{--}5) \text{ cm}^2/\text{V}\text{-sec}$. Thus, the carrier concentration in unintentionally doped films is $10^{12}\text{--}10^{13} \text{ cm}^{-3}$.

The effective intragrain minority carrier diffusion length in undoped nearly stoichiometric Zn_3P_2 films was measured by using the scanned electron beam induced current technique in an ETEC Autoscan electron microscope. In this technique, relatively large grains with flat surfaces are selected, and a silver Schottkey barrier is formed on the specimen so that the barrier covers a small portion of the grain under investigation. The scanning electron microscope was used to provide simultaneous measurement of beam position and current response as the electron beam was moved away from the edge of the Schottkey barrier. The magnitude of the induced current is proportional to $\exp(-x/L_e)$, where L_e is the effective diffusion length. When the electron beam was accelerated by 20 kV, the penetration is on the order of 2-3 μm . Thus, the carrier generation volume has a pencil-like shape with a length of about 0.45 μm and a width of about 0.1 μm . Since the grains under investigation have a dimension of about 5 μm , the scanned electron beam technique is valid for the measurement of effective intragrain diffusion length. Figure 10 shows an induced current-beam position relation, where the effective intragrain diffusion length is about 0.55 μm .

The in-situ doping of Zn_3P_2 films with acceptors, such as silver, during the CVD process was difficult. For example, silver chloride is thermally unstable in a hydrogen atmosphere, and the vapor pressure of elemental silver is too low for doping purposes. However, the dark resistivity of p-type zinc phosphide films may be reduced by adding hydrogen chloride or hydrogen bromide to the reaction mixture during the deposition process. The distribution of chlorine in the thickness

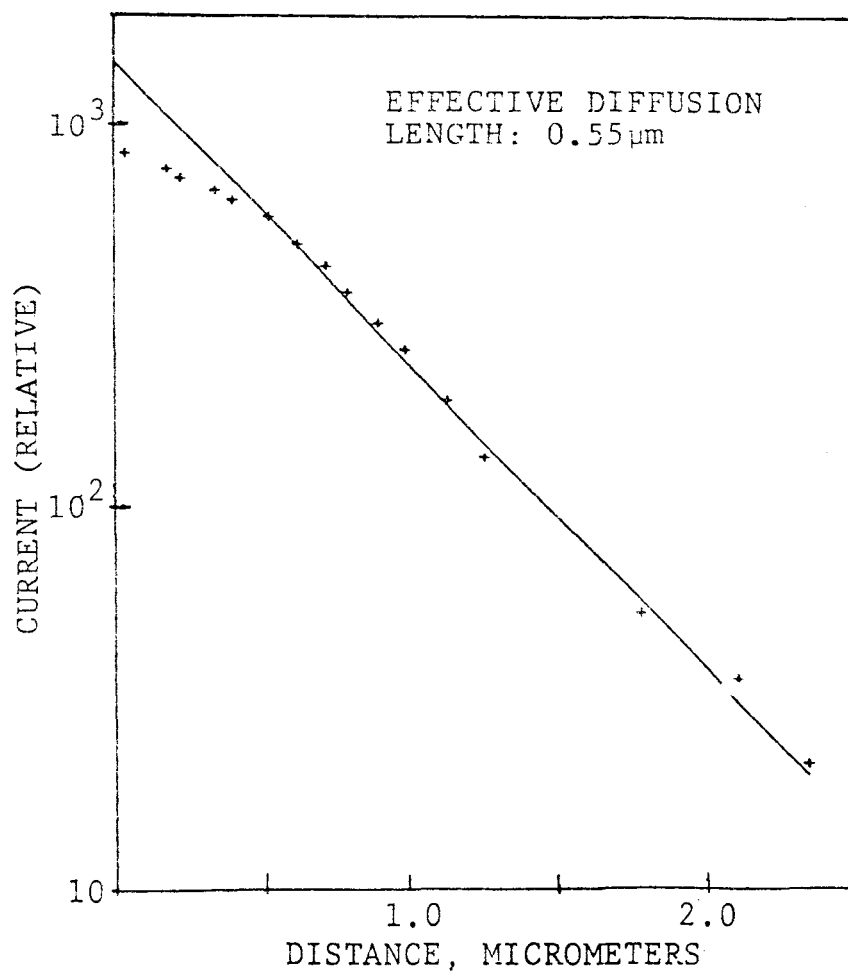


Fig. 10 The electron-beam induced current-beam position relation for the determination of effective intragrain diffusion length in an undoped zinc phosphide film.

direction of hydrogen chloride doped zinc phosphide films was determined by the ion-probe technique. A typical plot showing the depth profile of phosphorus and chlorine as well as the background concentration of chlorine is shown in Fig. 11, where chlorine at a concentration of 0.01% to 0.1% appears to be uniformly distributed throughout the film. The dark resistivity of hydrogen chloride or hydrogen bromide doped zinc phosphide films is typically $(3-5) \times 10^4$ ohm-cm as compared with 10^6 ohm-cm for undoped stoichiometric films. The dark resistance of a Ag/Zn₃P₂ (HBr)/W/steel structure has been measured in the temperature range 25°-150°C, as shown in Fig. 12, and an activation energy of 0.32-0.35 eV was obtained. It is possible that bromine or chlorine, being deep acceptors, compensates any shallow donors in zinc phosphide, thus reducing its dark resistivity.

To better control the electrical resistivity of CVD Zn₃P₂ films, a simple technique using a silver nitrate solution was developed. A silver nitrate solution of known concentration and volume was applied uniformly to the substrate surface, and the solution slowly vaporized. The silver salt remaining on the surface decomposes and diffuses into zinc phosphide during the deposition process. Using 10^{14} or more silver atoms per cm² of substrate, the surface of deposited films appears to be considerably darker than that of undoped film, indicating that an excess of silver has diffused through the films. By using about 10^{13} atoms for cm² of substrate, the dark resistivity of Zn₃P₂ was 200-300 ohm-cm.

III.2. Deposition and Properties of Zinc Selenide Films

Since zinc phosphide can only be prepared in the form of p-type films, heterojunction structures must be used for thin film solar cells.

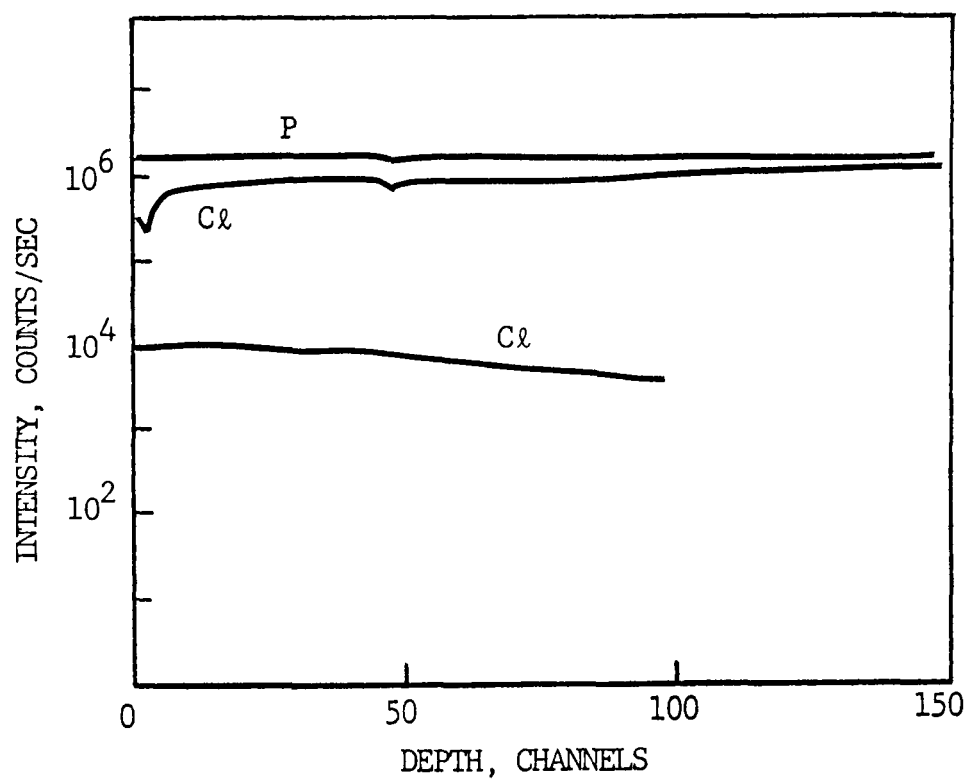


Fig. 11 Concentration profile of phosphorus and chlorine in the thickness direction of a hydrogen chloride-doped zinc phosphide film (the lower chlorine profile indicates the background concentration).

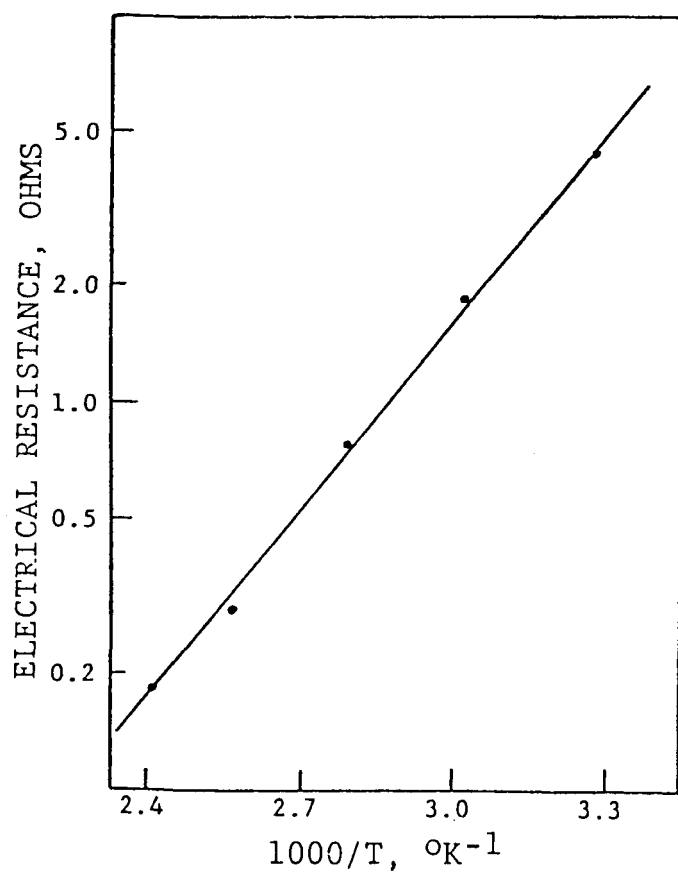


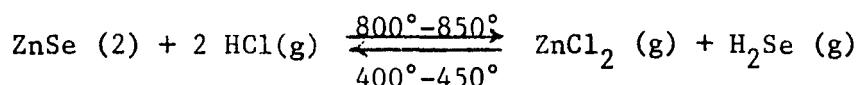
Fig. 12 The electrical resistance of a $\text{Ag}/\text{Zn}_3\text{P}_2 \cdot (\text{HBr})/\text{W}/\text{steel}$ structure as a function of temperature.

From energy gap and electron affinity considerations, n-ZnSe/p-Zn₃P₂ appears to be a suitable configuration (zinc selenide can only be prepared in the n-type form). The band gap of ZnSe is 2.7 eV. Although the growth of low resistivity n-type ZnSe crystals has been achieved by prolonged annealing of the crystal in a zinc atmosphere, the preparation of low resistivity ZnSe films, which is required for the preparation of efficient solar cells, is a different task. In this work, vacuum evaporation and chemical vapor deposition techniques were used for the deposition of ZnSe films.

In the evaporation technique, two types of source materials were used: (1) G.E. luminescent grade zinc selenide purified by heating in hydrogen at 800°C for 4 hours, and (2) zinc selenide synthesized by heating zinc, zinc, selenium, and aluminum (dopant) in a sealed fused ampoule at 850°C for two weeks. The technique of evaporation, i.e., the crucible configuration and heater arrangement, was the same as that used for evaporation of cadmium sulfide. Glass slides were used as substrates for convenience. The temperature of the substrate was maintained at 200°-250°, and the evaporation rate was 2-10 Å/sec. The resulting films, exhibited about 85% transmission at wavelength above 450 nm, were identified as ZnSe by microprobe analysis. Irrespective of the nature of the source material, substrate temperature, evaporation rate, and post-evaporation anneal in a zinc atmosphere, the sheet resistance of all films (3000-8000 Å thickness) was too high to be measured by the conventional four-point probe technique.

The chemical vapor deposition of zinc selenide films on Corning 7059 substrates was carried out by (1) the transport of zinc selenide with hydrogen chloride in a gas flow system and (2) the reaction of zinc

vapor with hydrogen selenide in a gas flow system. In the transport technique, G.E. luminescent grade polycrystalline zinc selenide or the zinc selenide synthesized from the elements was maintained at 850° C. A mixture of hydrogen and hydrogen chloride was passed over the source material in a fused silica reaction tube, and the resulting mixture was allowed to react on the surface of the substrate at 400° - 450° C. This process is based on the reversible chemical reaction between zinc selenide and hydrogen chloride as follows:



Adherent films of zinc selenide, as verified by microprobe analysis, were obtained. However, the deposition rate of zinc selenide was only about 1 µm/hr, and the sheet resistance of zinc selenide films was too high to be measured. The addition of indium chloride or aluminum chloride to the transport agent had no measurable effects on the sheet resistance of zinc selenide films.

The reaction between zinc vapor and hydrogen selenide in a hydrogen atmosphere was thought to be most promising since the Se/Zn solar ratio can be varied over a wide range. However, the deposited films at 400°-450°C were all of high resistivity containing 50.48 ± 1% Zn and 49.5 ± 1% Se. A typical EDS spectrum of a zinc selenide film is shown in Fig. 13.

III.3. Heterojunction Solar Cells

Many experiments have been carried out to prepare thin film zinc phosphide heterojunction solar cells. ITO/Zn₃P₂ cells, prepared by the ion beam sputtering of indium tin oxide onto the surface of Zn₃P₂/W/

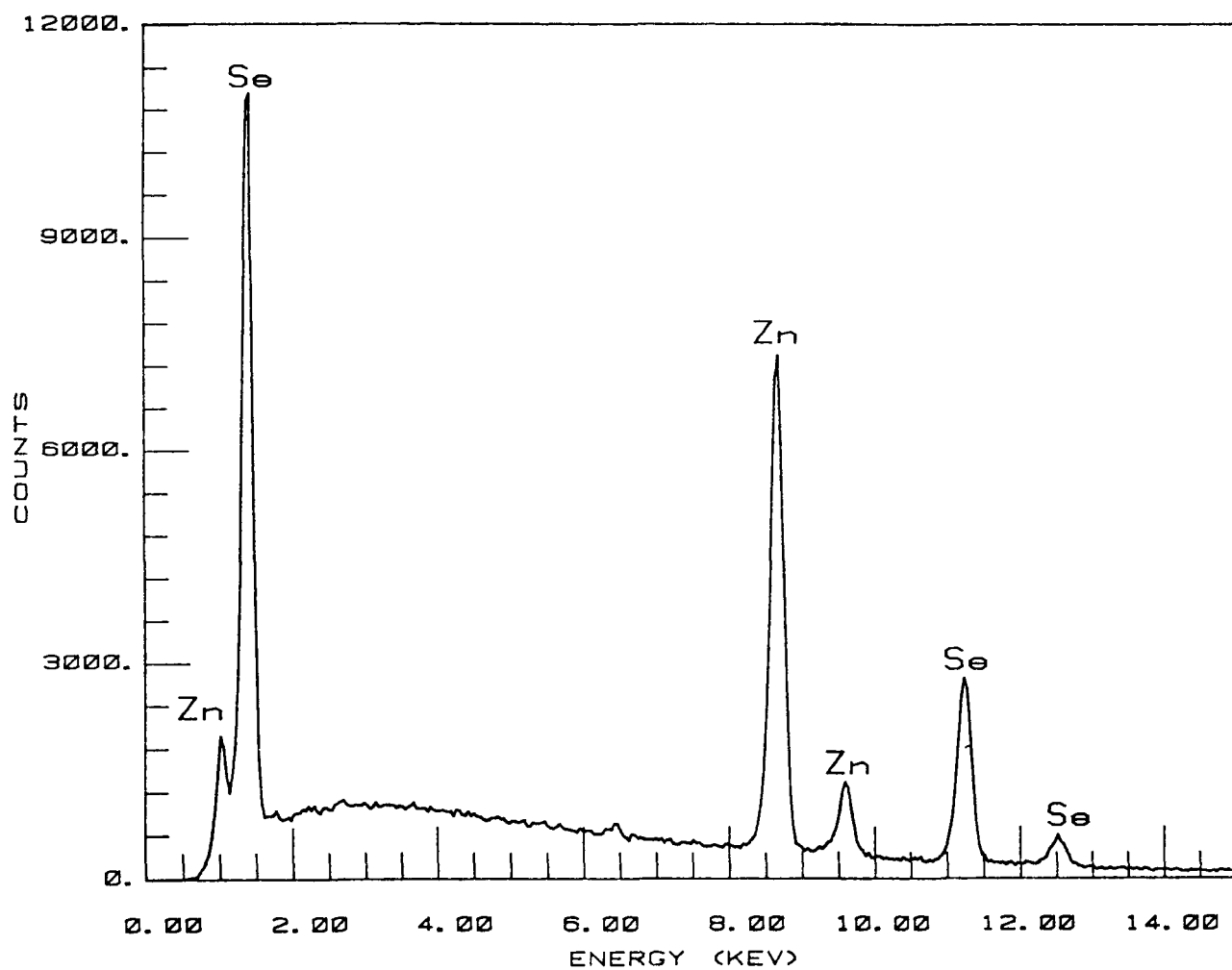


Figure 13 A typical EDS spectrum of a zinc selenide film deposited by the reaction of zinc vapor and hydrogen selenide at 450°C.

steel structures, showed relatively high short-circuit current density, up to 14 mA/cm^2 . However, these cells are unstable, and the photoresponse degrades rapidly. $\text{ZnSe/Zn}_3\text{P}_2$ thin film cells prepared by the successive in-situ deposition of Zn_3P_2 (8-10 μm) and ZnSe (2 μm) on W/steel substrates at 400-450°C are stable. The open-circuit voltage is up to 0.5 V; however, the short-circuit current density and fill factor are poor due to the high series resistance of the device. However, by depositing 3000 - 5000 Å of indium tin oxide film on $\text{ZnSe/Zn}_3\text{P}_2/\text{W}$ steel structures to reduce the series resistance, the open-circuit voltage is up to 0.6 V, and the short-circuit current density is increased to $2\text{-}3 \text{ mA/cm}^2$. Attempts to improve the solar cell characteristics by converting the surface region of Zn_3P_2 into Zn_3N_2 using ammonia treatment were not successful. The use of other window materials, such as zinc oxide and cadmium oxide, also did not produce improved photovoltaic characteristics. It is felt that the problems involved in the preparation of efficient thin film zinc phosphide solar cells are better suited for long-term projects, and the zinc phosphide work will be temporarily suspended in this program.

IV. Plan for the Next Period

1. Optimization of the properties of p-type cadmium telluride films.
2. Reduction of the p-CdTe/substrate interface resistance.
3. Investigations of the window materials for heterojunction solar cells.
4. Preparation and characterization of front wall thin film heterojunction cadmium telluride solar cells using various window materials.
5. Preparation and characterization of back wall cadmium telluride thin film solar cells.