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Thin Film Cadmium Telluride, Zinc Telluride, and Mercury Zinc Telluride Solar Cells

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SUMMARY

The major objectives of this program on thin film solar cells, supported by the Solar Energy Research Institute under Subcontract XL-8-18091-1, are to demonstrate (1) thin film cadmium telluride solar cells with a quantum efficiency of 75% or higher at 0.44 μm and a photovoltaic efficiency of 11.5% or greater, and (2) thin film zinc telluride and mercury zinc telluride solar cells with a transparency to sub-bandgap radiation of 65% and a photovoltaic conversion efficiency of 5% and 8%, respectively.

Efforts during the first year have been directed to (1) the deposition of CdTe films by close-spaced sublimination (CSS) and metalorganic chemical vapor deposition (MOCVD) techniques, (2) the deposition of transparent conducting semiconductor (TCS) films by solution-growth and MOCVD techniques, (3) the preparation and evaluation of thin film CdTe solar cells, and (4) the deposition and characterization ZnTe films and heterojunctions.

The deposition of CdTe films on glass and SnO_2/glass substrates at 370° - 380°C by MOCVD using the reaction between dimethylcadmium (DMCd) and diisopropyltellurium (DITe) in a H_2 atom has been investigated. The deposited film was identified as CdTe by electron microprobe and x-ray diffraction techniques. The optical bandgap of MOCVD CdTe films was measured to be 1.50 eV. The conductivity type of, and, to a limited extent, carrier concentration in deposited CdTe films can be controlled by controlling the DMCd/DITe molar ratio in the reaction mixture. This technique is promising for the preparation of thin film CdTe homojunction solar cells.

The deposition of CdS films from aqueous solutions has been investigated in detail using the reaction between thiourea and cadmium acetate in an ammonical solution (with an ammonium salt or triethanolamine added in some cases). The CdS films deposited on glass substrates are usually amorphous and those on SnO_2/glass substrates are of hexagonal structure with the grown surface parallel to the basal plane. The deposited CdS films show good optical transmission in the above-bandgap region; however, they are porous and impure, as shown by dissolution rate measurements. Heat treatment can be used to densify the solution-grown films, but cannot remove impurities. The dissolution rate of annealed, solution-grown CdS films is about one hundred times higher than that of CdS films deposited by vacuum evaporation. As a result, the photovoltaic characteristics of solar cells prepared from solution-grown CdS films are inferior to those prepared from vacuum evaporated CdS films.

The MOCVD technique has been used for the deposition of ZnO and ZnS films, two important TCSs, and of ZnTe films. ZnO films were deposited by the oxidation of diethylzinc (DEZn), and ZnS films by the reaction of DEZn with hydrogen sulfide. Their electrical and optical properties were measured. ZnTe films were deposited on glass, ZnO/SnO_2/glass, and ZnS/SnO_2/glass substrates at 370° - 380°C by the reaction between DEZn and diethyltellurium (DETe) in a H_2 atm. The deposited films are always p-type, and their resistivity can be controlled to a limited extent by varying the DEZn/DETe molar ratio in the reaction mixture. ZnO/ZnTe and ZnS/ZnTe heterojunctions have been prepared by the successive in-situ deposition of the TCS and ZnTe on SnO_2/glass substrates. Preliminary experiments indicated an open-circuit voltage of 0.6 - 0.7 V for ZnS/ZnTe heterojunctions.

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SECTION 1.0

INTRODUCTION

This is the Annual Technical Progress Report of a research program "Thin Film Cadmium Telluride, Zinc Telluride, and Mercury Zinc Telluride Solar Cells" covering the period July 1988 to June 1989 supported by the Solar Energy Research Institute under Subcontract XL-8-18091-1. The major objectives of this contract are to demonstrate (1) thin film cadmium telluride solar cells with a quantum efficiency of 75% or higher at 0.44 μm and a photovoltaic efficiency of 11.5% or greater, and (2) thin film zinc telluride and mercury zinc telluride solar cells with a transparency to sub-bandgap radiation of 65% and a photovoltaic conversion efficiency of 5% and 8%, respectively.

Thin film polycrystalline cadmium telluride is a promising photovoltaic material. Heterojunction solar cells with AM1 efficiencies higher than 10% have been prepared by several techniques. The configuration of the solar cell used in this program is:

Ohmic contact/p-CdTe/TCS/SnO_2:F/glass(substrate)

where TCS is the transparent conducting semiconductor. Since essentially all known TCSs are n-type, p-type CdTe must be used as the absorber. The solar cell is prepared by the successive deposition of the TCS, p-CdTe film, and ohmic contact on SnO_2:F coated glass substrates. The problems associated with the use of p-CdTe films are well known: the difficulty of depositing high conductivity films owing to self-compensation and the difficulty of forming low-resistance ohmic contacts owing to the large work function of p-CdTe. The important parameters determining the photovoltaic characteristics of the solar cell are:

- The electrical resistivity and homogeneity of p-CdTe.
- The ohmic contact/p-CdTe interface resistance.
- The bandgap energy, electrical resistivity, electron affinity, lattice parameter, and thermal expansion coefficient of TCS.
- The cleanliness of the p-CdTe/TCS interface.

During the past year, efforts have been directed to the following tasks:

- The deposition of TCS films from aqueous solutions, with particular emphasis on CdS.
- The optimization of the close-spaced sublimation process for better reproducibility of low resistivity p-CdTe films.
- The deposition of p-CdTe films by MOCVD for comparison with CSS films.
- The preparation and characterization of thin film CdS/CdTe solar cells for optimization of CdS deposition.
- The deposition and characterization of ZnTe films and ZnTe/TCS junctions.

The experimental procedures used in these tasks and the results obtained are discussed in the following sections.

SECTION 2.0

DEPOSITION AND CHARACTERIZATION OF p-CdTe FILMS

Several techniques have been developed for the deposition of CdTe films, including close-spaced sublimation (CSS), chemical vapor deposition (CVD), spray pyrolysis, electrodeposition, and metalorganic chemical vapor deposition (MOCVD). The CSS, CVD (direct combination of vapors of elements) and spraying techniques require relatively high temperatures, 500°C or above. The electrodeposition is a low temperature process; however, the composition of deposited CdTe films cannot be readily controlled. The MOCVD technique is a low temperature process and is, in principle, capable of controlling the composition of deposited CdTe films. However, the control of dopant concentration and distribution in polycrystalline CdTe films has not been explored. The use of low temperatures is advantageous in that self-compensation and native defects can be reduced and that the absorber-window interface reactions can be minimized.

In this program, CSS is the major technique used for the deposition of CdTe films. As a continuation of the previous program on thin film CdTe solar cells [1], this process has been further investigated. In addition, the MOCVD technique has been explored for the deposition of CdTe films of controlled dopant concentration for the preparation of junction structures. It is believed that the results on MOCVD CdTe solar cells could provide information on the ultimate efficiency of thin film solar cells.

2.1 CLOSE-SPACED SUBLIMATION (CSS)

The deposition of CdTe films by the closed-spaced sublimation (CSS) technique is based on the reversible dissociation of CdTe at high temperatures:

$$2\ CdTe(s) \rightleftharpoons Cd(g) + Te_2(g)$$

The source material is maintained at a higher temperature than the substrate. The source CdTe dissociates into its elements, which recombine on the substrate surface depositing CdTe films. The dissociation pressure of CdTe at a given temperature is defined by the relation:

$$K_{CdTe}(T) = (p^{\circ}_{Cd})\ (p^{\circ}_{Te_2})^{1/2}$$

where the p°'s are the equilibrium partial pressures at temperature T. The p°'s increases exponentially with increasing temperature. The equilibrium partial pressure of Te_2 has been calculated to be 2.6×10^{-7}, 7.8×10^{-6}, and 1.2×10^{-4} atm at 500°, 600°, and 700°C, respectively (the equilibrium partial pressure of Cd at a given temperature is twice of that of Te_2). Thus, the rate of CdTe deposition depends strongly on the source temperature and the gas pressure in the reaction tube.

2.1.1 THE DEPOSITION PROCESS

The source material for the deposition of CdTe films by the CSS technique was prepared by the direct combination of the elements in a sealed fused silica tube. The reaction mixture was Cd-deficient with a Cd vacancy concentration of about 10^{19} cm^{-3} or doped with As or Sb to a similar concentration. The synthesized CdTe was pulverized and placed in a shallow, silicon carbide - coated graphite crucible, which was used as the source material for the deposition of CdTe films. The substrates used for the deposition of CdTe films were: Corning 7059 glass, SnO_2:F/glass (sheet resistance of about 10 ohms per square, prepared by the thermal oxidation of tetramethyltin with oxygen using Freon as a dopant), and TCS/SnO_2:F/glass (the SnO_2:F films were used to reduce the sheet resistance of the TCS film).

The apparatus used for the deposition of CdTe films by the CSS technique is shown schematically in Fig. 2-1. The substrate and source, separated by about 0.1 cm and supported by appropriate holders, were enclosed in a controlled atmosphere in a fused silica tube provided with gas inlet and outlet tubes. They were maintained at desired temperatures by using quartz lamps,and thermocouples inserted into the holders were used to control their temperatures (due to the location of the thermocouples, the true temperature of the source is lower than the temperature indicated by the thermocouple, and that of the substrate is higher than the temperature indicated by the thermocouple). Since the spacing between the source and substrate is less than a few percent of the dimension of the substrate, the material transport conditions are largely independent of conditions elsewhere in the system. The CSS process is essentially diffusion-limited, and the close-spacing of source and substrate provides direct transport of each component of the source across the space to the substrate.

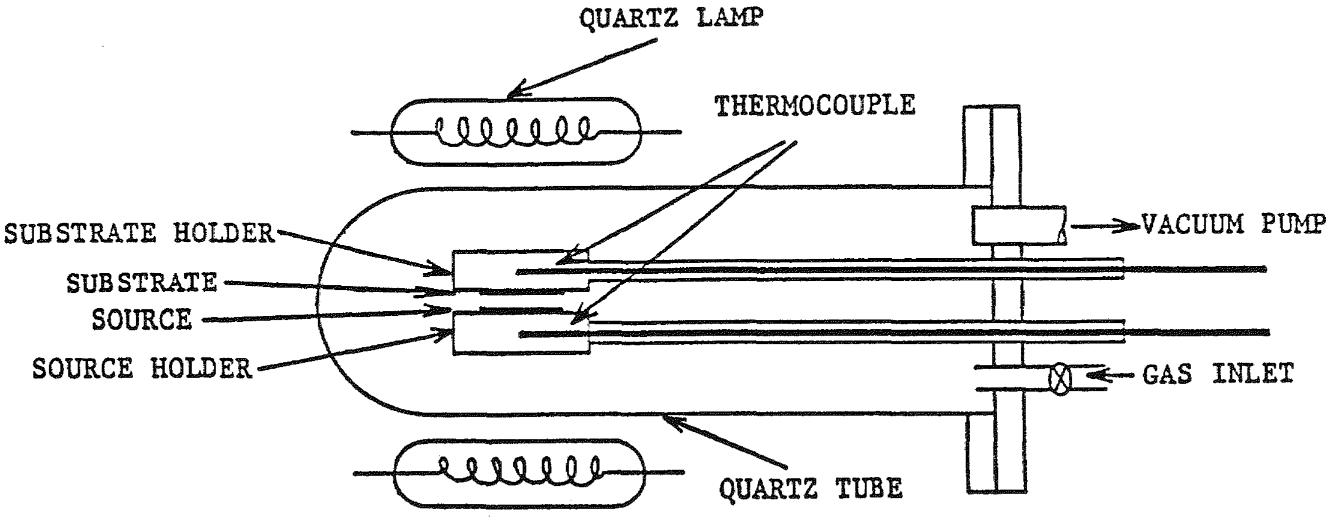


Figure 2-1. Schematic diagram of the apparatus for the deposition of CdTe films by the CSS technique.

The CSS technique involves several interrelated parameters, such as the temperatures of the source and the substrate, the separation between the source and the substrate, the nature of the atmosphere and the pressure in the reaction tube, the composition of the source material, etc. For example, the pressure in the reaction tube is important in determining the rate of deposition, since the dissociation pressure of CdTe depends exponentially on temperature. At a given source temperature, the sublimation rate increases rapidly as the pressure in the reaction tube is reduced from the atmospheric pressure.

The feasibility of using junction photovoltage (JPV) spectroscopy to evaluate the effects of process parameters on the properties of CSS CdTe films was investigated. A Polaron Model 4200 electrochemical profiler with a photovoltage attachment in the wavelength range of 500 - 900 nm was used. Polycrystalline CdTe with a Cd vacancy concentration of 10^{19} cm^{-3}, prepared by direct synthesis, was used as the source material. CdS films deposited on SnO_2:F coated glass (see Section 3.0) were used as substrates. CdTe films were deposited on the substrates in the temperature range of 600° - 640°C with a source-substrate temperature difference of 80°C. Contacts were then made to the SnO_2 and as-grown surface, and the junction photovoltage spectrum measured in the open-circuit mode. The results are shown in Figure 2-2, where the area under the curve represents the open-circuit voltage under the illumination level of the instrument. The result that the junctions prepared at 625° - 630°C showed considerably higher JPV than the junction prepared at 600°C is difficult to understand, since the reaction between CdS and CdTe becomes more pronounced as the deposition temperature is increased.

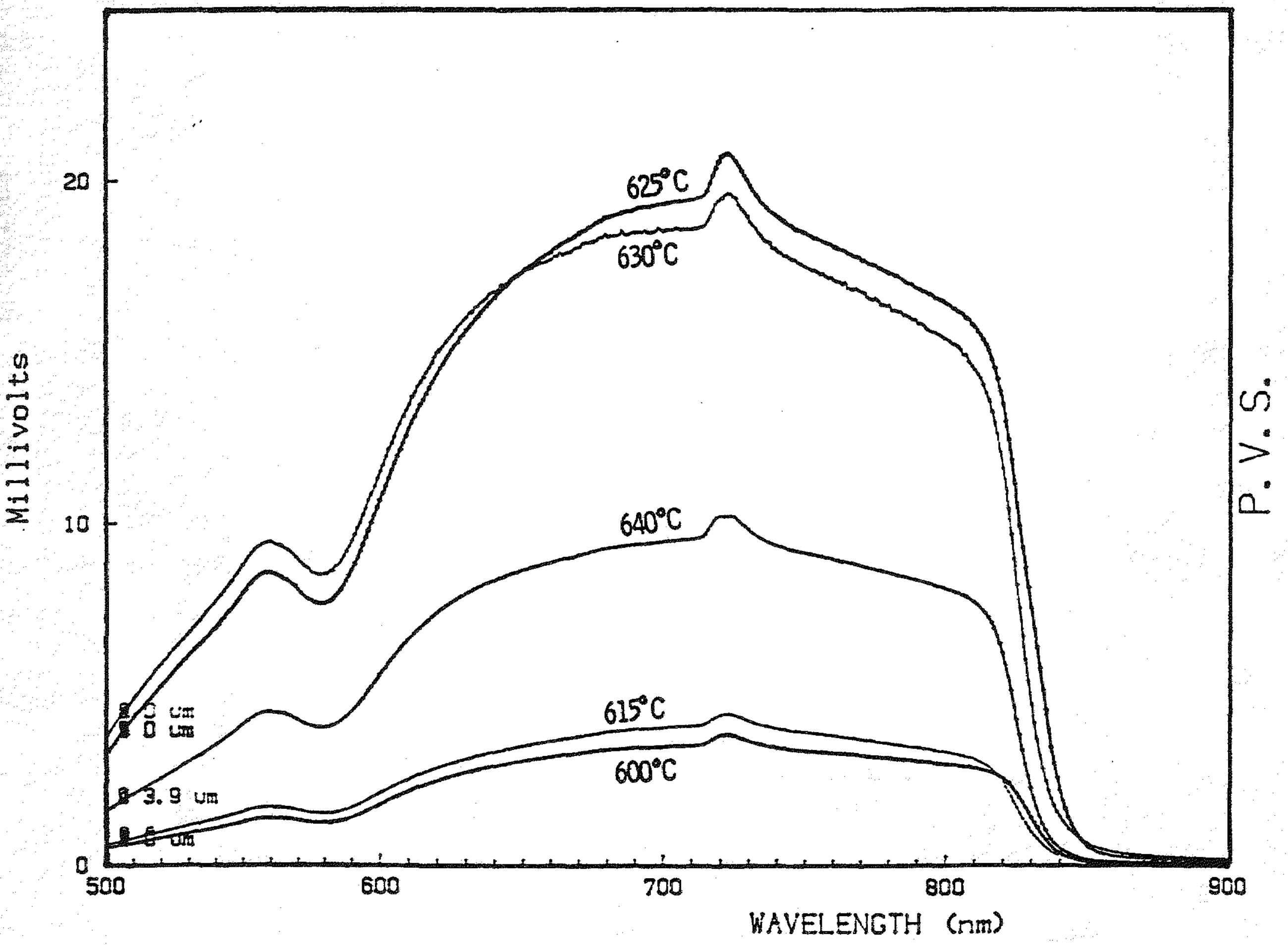


Figure 2-2. Photovoltage spectra of CdS/CdTe junctions prepared at various temperatures.

2.1.2 MICROSTRUCTURE

The microstructure of CdTe films is determined by the substrate temperature, source-substrate temperature gradient, and the crystallinity of the substrate. In general, the grain size increases with increasing substrate temperature and increasing film thickness, and the grains become more closely packed at small source-temperature gradient due to reduced deposition rate. The effect of the crystallinity of the substrate on the grain structure is illustrated in Figure 2-3, where the scanning electron micrographs of CdTe films deposited on glass and CdS/SnO_2/glass substrates at 600°C (source temperature 680°C) in the same experiment are shown. CdS is polycrystalline; the deposited CdTe film consists of closely-packed crystallites while the crystallites in the CdTe film on the glass substrate are clearly distinguishable. Further, X-ray diffraction data indicate that the CdTe film on glass is essentially polycrystalline and that the CdTe film on CdS/SnO_2/glass shows a strong preferred (111) orientation.

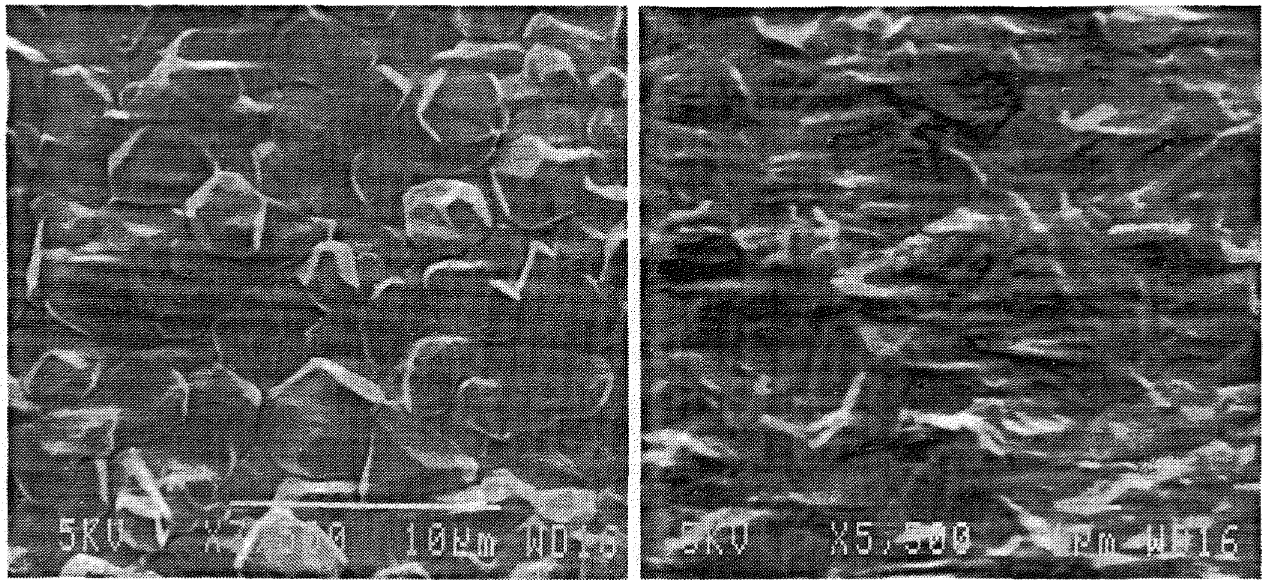


Figure 2-3. Scanning electron micrographs of CdTe films deposited on glass (left) and CdS/SnO_2/glass (right) substrates at 600°C.

2.1.3 ELECTRICAL RESISTIVITY

The electrical resistivity of CSS p-CdTe films is a most important property affecting the photovoltaic characteristics of solar cells. The resistivity of CdTe films is determined by the substrate temperature, substrate-source temperature gradient, and the composition of the source material. The process parameters developed in the previous program were [1]: the source material doped extrinsically or intrinsically to a concentration of 10^{19} Sb atoms or Cd vacancies per cm^3, a substrate temperature of 600°C, and a source temperature of 700°C. P-CdTe films of 300-500 ohm-cm resistivity were reproducibly deposited at rate of 6-8 μm/min. This high rate of deposition has been found to produce films with loosely-packed grains, similar to those deposited on glass substrates, shown in Figure 2-3. To improve the microstructure of CdTe films, the source-substrate temperature gradient must be reduced. The optimum substrate temperature is about 600°C, since the reaction between CdTe and CdS becomes more pronounced at higher temperatures and the microstructure of CdTe degrades at lower temperatures. By reducing the source temperature to 680°C, the deposition rate is reduced to 1 - 1.2 μm/min., and the deposited films showed significantly improved microstructure (Figure 2-3).

To measure the electrical resistivity of p-CdTe films deposited on SnO_2:F/glass or CdS/SnO_2:F/glass substrates, Au-Cu contacts were applied to the film surface at 150° - 180°C by using a $AuCl_3$-$CuCl_2$ solution. Since the CdTe/SnO_2 or CdTe/CdS interface is rectifying, the upper limit of the resistivity may be deduced from the forward characteristics of the junction structures at large bias. Many p-CdTe films have been deposited on CdS/SnO_2:F/glass substrates at 600°C using source materials with Cd vacancy or Sb concentration of 10^{19} cm^{-3}, maintained at 680°C. The resistivities of the CSS p-CdTe films have not been reproducible, many of these films were found to have resistivities higher than 1000 ohm-cm, considerably higher than the resistivity of films deposited at 600°C from a source at 700°C. It is likely that the impurities in CdS films deposited from aqueous solutions (see Section 3.0) contribute dopants to CdTe. The process parameters of the deposition process are under investigation to reduce the resistivity of p-CdTe films.

2.2 METALORGANIC CHEMICAL VAPOR DEPOSITION (MOCVD)

The MOCVD of II-VI compounds is still in its infancy as compared with that of III-V compounds. Two review papers have summarized the earlier work on the MOCVD of narrow gap and wide gap II-VI compounds [2,3], and significant progress has been made recently concerning the homoepitaxial growth of CdTe and the heteroepitaxial growth of $Hg_{1-x}Cd_xTe$ on CdTe substrates [4,5]. The reaction of an organocadmium compound, such as dimethylcadmium (DMCd), and an organotellurium compound, such as diethyltellurium (DETe) or diisopropyltellurium (DITe), is commonly used for the deposition of CdTe on the surface of heated substrates. The thermal instability of these organic compounds permits the use of relatively low temperature, 350°C for example, for the deposition process. The development of Cd and Te compounds of greater instability will further reduce the deposition temperature.

2.2.1 THE DEPOSITION PROCESS

The reaction between DMCd and DITe in a hydrogen atmosphere has been used for the deposition of CdTe films using the apparatus shown schematically in Figure 2-4. The flow of various gases was directed by appropriate valves and controlled by mass flow controllers. The metalorganic compounds are liquid at room temperature with vapor pressures of 25 and 1.5 Torr for DMCd and DITe, respectively, at 20°C. They were carried into the reaction tube by bubbling measured amounts of hydrogen through the liquids. The reaction mixture was then introduced into a fused silica reaction tube of 5.5 cm ID, in which the substrates were supported on a susceptor and the susceptor heated externally by an rf generator. Glass and SnO_2:F coated-glass were used as substrates. The important process parameters are the substrate temperature, and the composition and flow rate of the reaction mixture. The substrate must be maintained at such temperatures that SnO_2 is not reduced by hydrogen while the reaction rate between DMCd and DITe is sufficiently high to permit the deposition of CdTe at reasonable

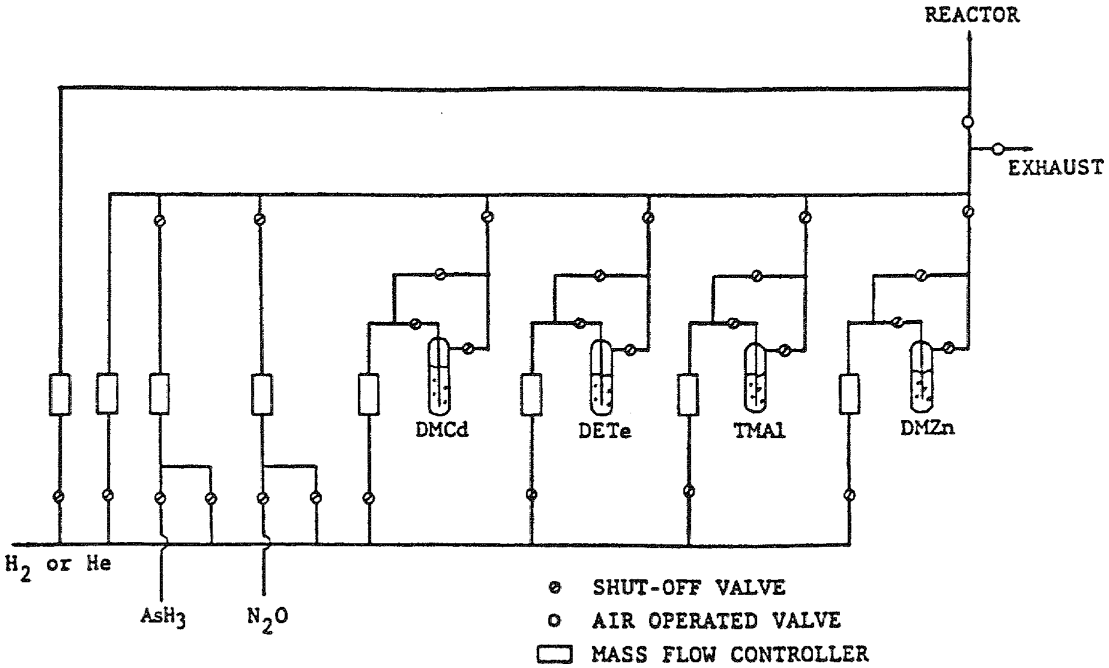


Figure 2-4. Schematic diagram of the apparatus for deposition of CdTe films.

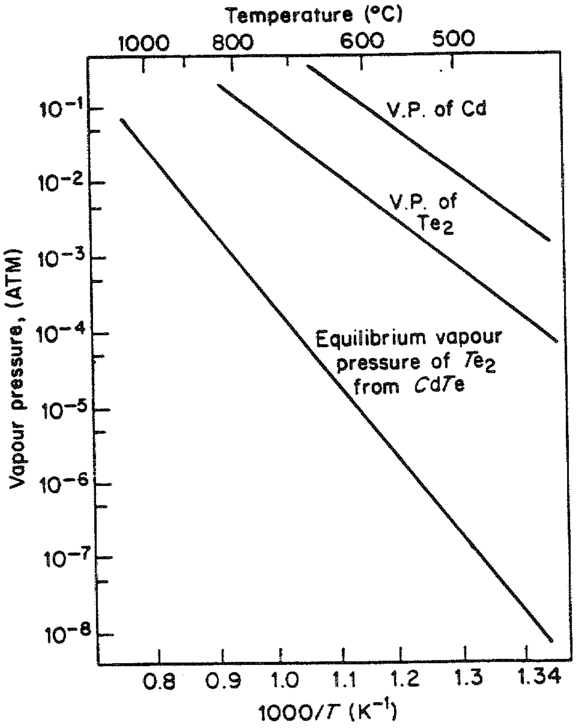


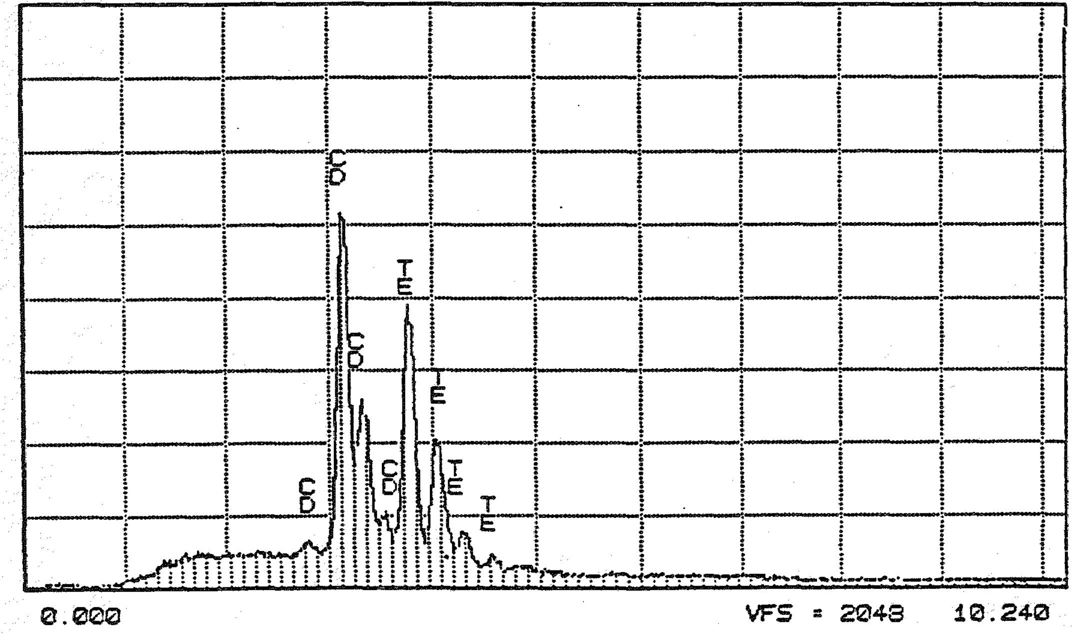
Figure 2-5. Equilibrium vapor pressures of Te_2 from the dissociation of CdTe and the equilibrium vapor pressures of Cd and Te_2.

rates. Because of the use of relatively low substrate temperatures, the composition of the reaction mixture is important in that no free Cd or Te_2 deposits on the substrates. Figure 2-5 shows the equilibrium vapor pressure of Te_2 from the dissociation of CdTe and equilibrium vapor pressures of Cd and Te_2. DMCd is known to be more stable than DITe, and the decomposition of DITe on the substrate surface takes place to a greater extent than that of DMCd. If an excess of DMCd or DITe is present in the reaction mixture, the partial pressure of that element must be less than its equilibrium vapor pressure at the substrate temperature. Otherwise, that element will deposit on the substrate surface leading to poor electrical and structural properties. Further, the deposition conditions must be so adjusted that the formation of CdTe takes place on the substrate surface, since the deposition of CdTe particles, formed in the gas phase, on the substrate surface yields non-adherent deposits.

The results of several deposition experiments indicate that the maximum substrate temperature which can be used without the reduction of SnO_2 is 370°-380°C. In most experiments, the flow rates of hydrogen and DITe were 0.1 and 2.6×10^{-5} moles/min, respectively, and the flow rate of DMCd was varied to provide DMCd/DITe molar ratios in the range of 0.8 - 2.5. The deposition rate of CdTe was 1-2 μm/hr., depending on the composition of the reaction mixture.

2.2.2 PROPERTIES

The CdTe films deposited by MOCVD are adherent to the substrate and are essentially stoichiometric within experimental errors of electron microprobe analysis. The results of a typical analysis are shown in Figure 2-6.



Element	K-ratio	Z	A	F	Atom%	Wt%
Cd-L	0.477	0.971	1.018	0.982	49.48	46.32
Te-L	0.465	1.027	1.124	1.000	50.52	53.68
					Total=	100.00%

Figure 2-6 Electron microprobe analysis of a MOCVD CdTe film.

The crystallographic properties of CdTe films deposited on glass substrates were examined by the x-ray diffraction technique using Cuk_d radiation. Polycrystalline CdTe 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 1.945 Å, and relative intensities of 100, 62, and 28, respectively. The diffraction spectra of MOCVD CdTe films were obtained by scanning 2θ in the range of 20° - 60°. One typical spectrum is shown in Figure 2-7, where the film shows a strong {111} preferred orientation.

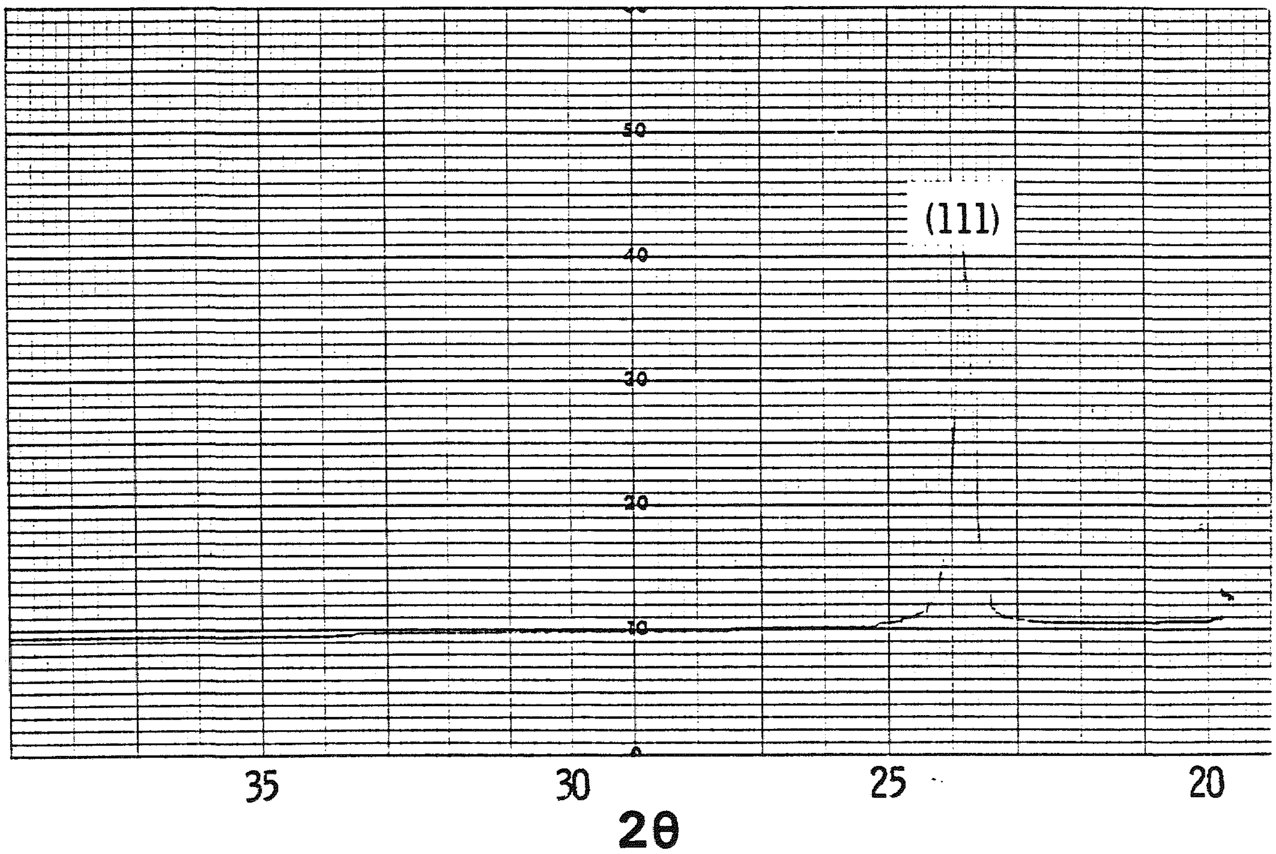


Figure 2-7 X-ray diffraction spectrum of a MOCVD CdTe film.

The optical absorption of CdTe films deposited on glass substrates was measured at room temperature using a Varian Model Cary 17D spectrophotometer. Figure 2-8 shows a plot of the square of the absorption coefficient versus photon energy. The extrapolation of the linear portion of the plot to the energy axis yields an optical bandgap of 1.5 eV for the fundamental absorption, essentially the same as the bandgap energy of single crystalline CdTe.

The electrical resistivity of MOCVD CdTe films on glass substrates was measured by the four-point probe technique. At DMCd/DITe molar ratios greater than about 1.5, the deposited films appear to be n-type, and the resistivity decreases with increasing DMCd/DITe molar ratio, as shown in Figure 2-9. The films become p-type at DMCd/DITe molar ratios below about 0.8.

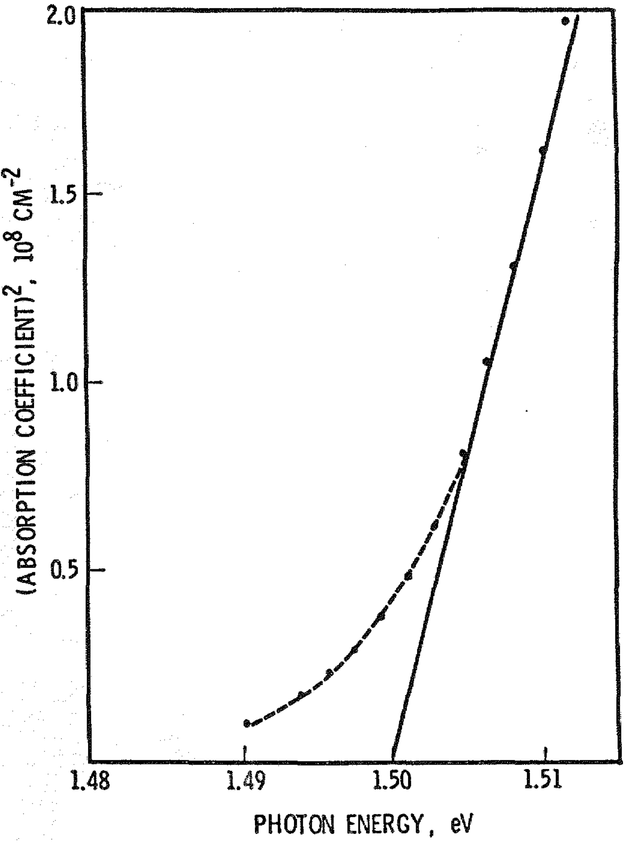


Figure 2-8 Optical absorption data of a CdTe film.

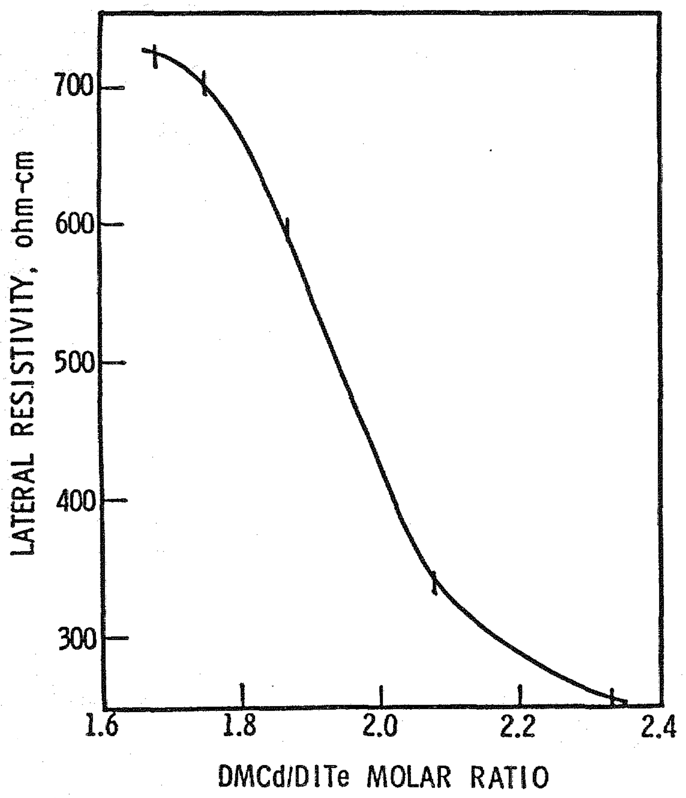


Figure 2-9 Resistivity of n-type MOCVD CdTe films.

The MOCVD CdTe films deposited on SnO_2/glass substrates were examined by the surface photovoltage (SPV) technique. The effects of the composition of the reaction mixture on SPV is shown in Figure 2-10. It is believed that these results could have been affected by surface states.

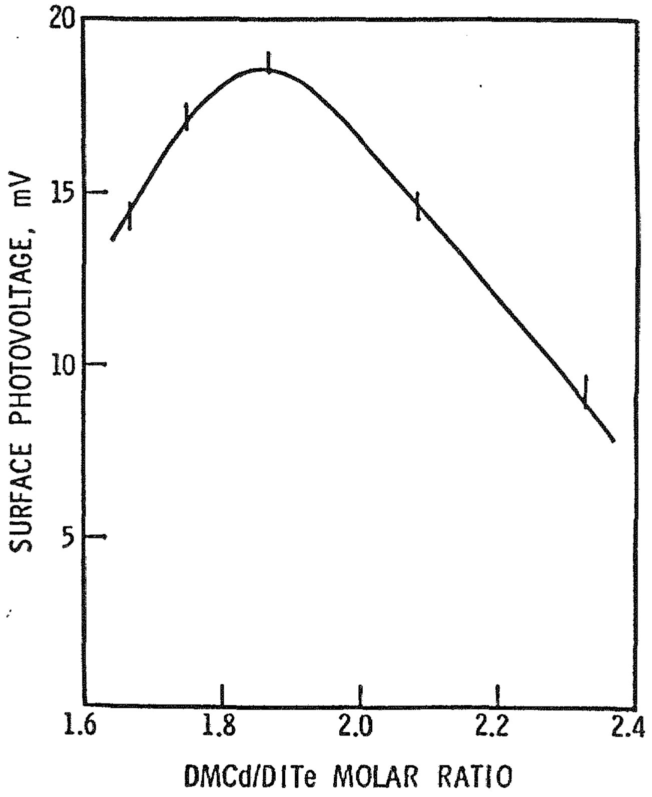


Figure 2-10 Surface photovoltage of MOCVD CdTe films as a function of composition of reaction mixture.

SECTION 3.0

TRANSPARENT CONDUCTING SEMICONDUCTOR FILMS

High conductivity large band-gap semiconductor films have major applications in many active and passive electronic and opto-electronic devices. The TCSs are mainly non-stoichiometric or doped oxides and sulfides. The deposition, properties, and applications of several TCS films, such as tin oxide, indium oxide, zinc oxide, cadmium stannate, etc. have been the subject of several reviews [6,7]. For heterojunction solar cells, the electron affinity, lattice parameter, and thermal expansion coefficient of the TCS should be similar to those of the absorber. Any difference in electron affinities of the absorber and the TCS will result in band discontinuities. The mismatch in lattice parameters and thermal expansion coefficients will result in interface states.

The properties of CdTe and several TCSs are summarized in Table 3-1. Cadmium sulfide is a commonly used window material for efficient thin film CdTe solar cells. The electron affinity of CdS is higher than that of CdTe; there is no spike in the conduction band to impede the transport of minority carriers (electrons) from p-CdTe to the TCS. However, the bandgap energy of CdS is only 2.42 eV, and 0.1 μm of CdS films will absorb 36% of the incident radiation with energy greater than the bandgap energy. Thus, a larger bandgap TCS is desirable as long as its electron affinity is higher than that of CdTe. Among large band-gap oxides, ITO with larger bandgap energy and electron affinity is not entirely satisfactory because of its reactivity toward CdTe at high temperatures used in the deposition process (ITO deposited by ion-beam sputtering has been used

Table 3-1. Properties of Selected II-VI Compounds and TCS.

Semiconductor	Energy Gap, eV	Lattice Constants, Å	TEC $\times 10^{-6}$ °C^{-1}	Electron Affinity, eV
CdTe (cubic)	1.50 (d)	6.477	5.5	4.28
CdSe (cubic)	1.74 (d)	6.05	4.8	4.8
ZnTe (cubic)	2.25 (d)	6.104	8	3.53
CdS (hex)	2.42 (d)	a = 4.137 c = 6.716	5.0 (⊥C) 2.5 (//C)	4.5
ZnO	3.3 (d)	a = 3.25 c = 3.21	4.8 2.9	4.35
ZnS (hex)	3.58 (d)	a = 3.819 c = 6.256	5.9-6.5 (//C) 4.5 (⊥C)	3.9
In_2O_3:Sn	3.7-4.4			4.5
SnO_2:F	3.9-4.6	6.7		4.8

successfully as the TCS for backwall CdTe cells). SnO_2 and ZnO are inert towards CdTe. Thin film SnO_2/CdTe junctions appear to have lower photovoltage than CdS/CdTe junctions [8], and thin film ZnO/ZnTe junctions have not been extensively studied. Thus a CdS is the only TCS used for efficient high V_{oc} thin film CdTe solar cells. An alternate approach to reduce the above-gap absorption of CdS films is to reduce its thickness. For example, the absorption of the above-gap radiation is reduced to approximately 20% and 13%, respectively, at thickness of 500 Å and 300 Å. Therefore, the deposition of large bandgap TCS as well as thin CdS films have been under investigation in this program.

3.1 CADMIUM SULFIDE FILMS.

The commonly used techniques for the deposition of CdS films include vacuum evaporation, chemical vapor deposition, chemical spraying, and solution growth. Evaporation from a CdS source in a conventional bell jar system is the standard deposition technique in the fabrication of Cu_2S/CdS solar cells. This technique was used for the deposition of CdS films in the previous program [1], where luminescent grade CdS powder in a graphite crucible was heated at about 800°C using a tantalum resistance heater. The substrates held by a metal holder and heated radiatively were 30 - 50 cm from the source material. The carrier concentration in deposited CdS films, usually 10^{15} to $10^{16}cm^{-3}$, is determined by the parameters of the evaporation process, such as substrate temperature. Highly conductive films (carrier concentration of 10^{18} to 10^{19} cm^{-3}) can be deposited by the coevaporation of In.

Chemical vapor deposition technique using the reaction between elemental Cd or a volatile Cd compound with hydrogen sulfide in a gas flow has been used extensively for the growth of CdS films and crystals. The solution spray technique is better suited for larger scale applications. Typically, an aqueous solution containing equimolar $CdCl_2$ and thiourea of 0.01 M to 0.1 M concentration is used. The chemical reaction takes place when the solution is sprayed onto a heated substrate, depositing CdS. The properties of the deposited films depend on the substrate temperature, spraying rate, and post-spray heat treatment.

The deposition of CdS films on glass and coated glass substrates from aqueous solutions has been reported by several authors [9,10]. This deposition process is based on the reaction of a cadmium salt with thiourea on the substrate surface in an aqueous solution at 85° - 95°C. However, the chemical reaction also takes place in the solution precipitating CdS, and the absorption of CdS particulates on the substrate surface yields powdery and nonadherent films. Thus, the deposition conditions, such as the concentration of reaction species in solution, must be optimized to promote the surface reaction. This technique has the potential advantage of being a simple, low-cost and scalable method for the deposition of TCS films of controlled composition. However, the application of the solution growth technique to photovoltaic devices required detailed investigations.

The deposition of CdS films from an aqueous solution of a Cd salt, NH_4OH, and thiourea has been reported in detail [9]. The Cd^{++} reacts with NH_4OH to form white insoluble $Cd(OH)_2$ which dissolves in an excess of NH_4OH to form $Cd(NH_3)_4{}^{++}$. The relative quantities of $Cd(OH)_2$ and $Cd(NH_3)_4{}^{++}$ is thus determined by the concentration of NH_4OH in solution. It has been claimed that better quality CdS films were obtained from a turbid solution of the reaction mixture. This is believed to be unlikely because of the low reaction rate between $Cd(OH)_2$

particles and thiourea. To minimize the formation of $Cd(OH)_2$ precipitates, NH_4Cl can be added to the reaction mixture to suppress the concentration of OH^- in solution, thus the formation of $Cd(OH)_2$ [11]. Triethanolamine (TEA) has also been used to form a more stable Cd-complex in solution [12]. The properties of CdS films deposited by various chemical reactions have been evaluated by the x-ray powder diffraction, optical absorption, electrical resistivity, and other measurements. For example, using TEA as the complex agent, CdS was deposited at 50°C at a rate of 80 Å/min (reached a terminal thickness of 1.7 μm after about 5 hrs) and consisted of both hexagonal and cubic phases. However, there is only limited information regarding the use of solution-grown CdS films for photovoltaic devices [10]. Solar cells were fabricated by dipping CdS films on metal substrates in a cuprous chloride solutions to form a Cu_2S/CdS heterojunction. The best cell of 1 cm^2 area showed V_{oc}, J_{sc}, and η of 0.2 V ,2.7 mA/cm^2, and 0.13%, respectively, under AM1 illumination.

3.1.1 SOLUTION GROWTH PROCESS

Many experiments on the deposition of CdS films have been carried out under a wide range of experimental conditions. Briefly, an aqueous solution of $Cd(CH_3COO)_2$, an ammonium salt (chloride or acetate) or TEA, and NH_4OH was heated at 85° - 95°C, and glass or SnO_2/glass substrates, after ultrasonic cleaning with methanol and perchloroethylene, were suspended vertically in the solution, as shown in Fig. 3-1. With constant stirring, an aqueous solution of thiourea was

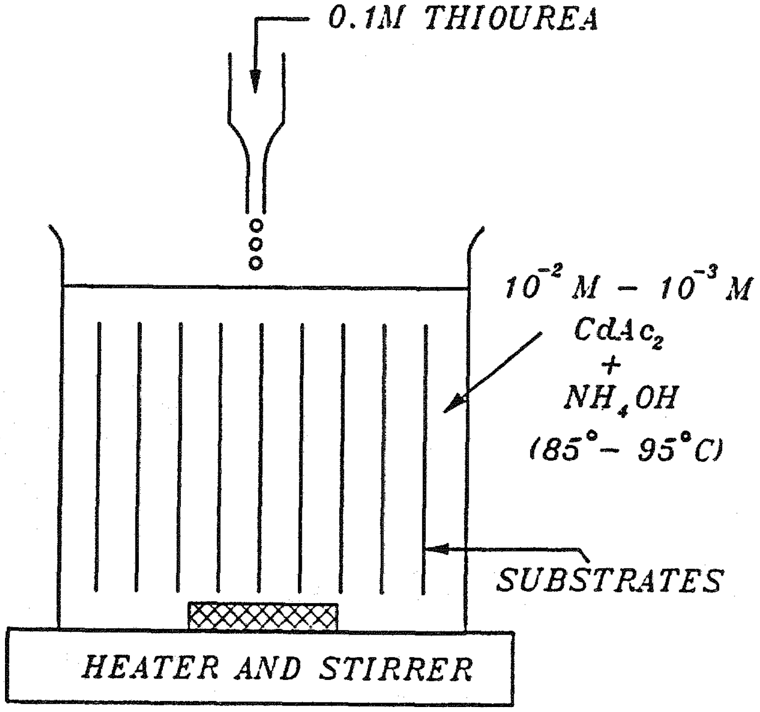


Figure 3-1 Schematic of the apparatus for the deposition of CdS films from an aqueous solution.

gradually added to the solution. Initially, the formation of CdS films takes place predominately on the substrate surface, and the solution turns turbid. Further addition of thiourea yields voluminous orange precipitates of CdS in the solution. The concentration of the cadmium salt is an important factor determining the deposition rate and properties of CdS films, concentrations in the range of 10^{-2} to 10^{-3} M were found to be suitable. Adherent films were deposited under a wide range of conditions at rates of 40 - 100 Å/min, and films deposited on SnO_2/glass substrates were more adherent than those on glass substrates, as shown by the Scotch tape test. Further, CdS films of 1000 Å or less in thickness deposited on glass substrates over a wide range of deposition rates were discontinuous, as shown in Figure 3-2. This is due to the fact that the nucleation of CdS on the smooth surface of the glass substrates is difficult. Once the nuclei are formed, further deposition tends to continue the growth of the initial nuclei rather than initiating nucleation. The nucleation of CdS on SnO_2/glass substrates takes place more readily; however, films deposited on SnO_2/glass substrates at low rates, such as 40 Å/min, were usually discontinuous. Continuous films were obtained at higher deposition rates, such as 100 Å/min.

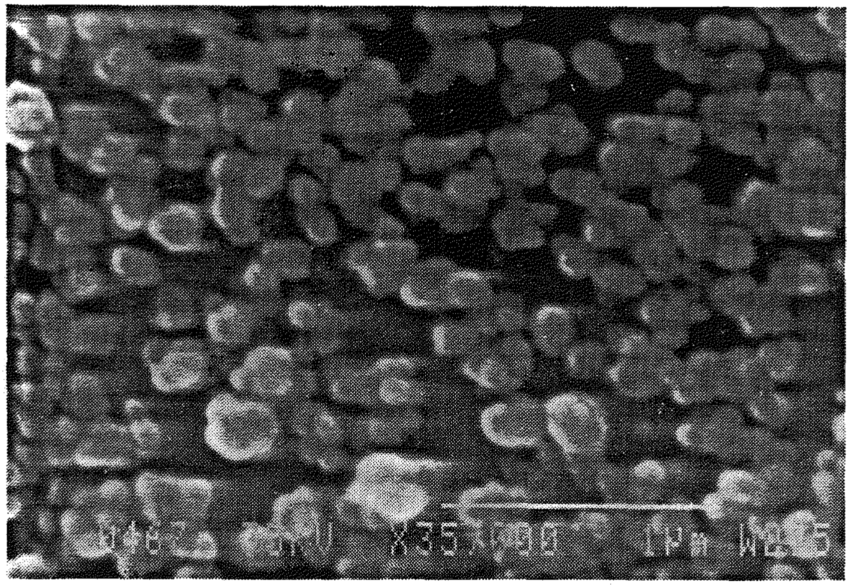


Figure 3-2 Scanning electron micrograph of a CdS film deposited on a glass substrate from solution.

3.1.2 OPTICAL TRANSMISSION

The optical absorption of solution-grown CdS films was measured using Varian Model Cary 17D spectrophotometer. The films deposited from solutions of various compositions showed essentially the same absorption characteristics. Figure 3-3 shows the transmission spectra of two solution-grown CdS films of 550 and

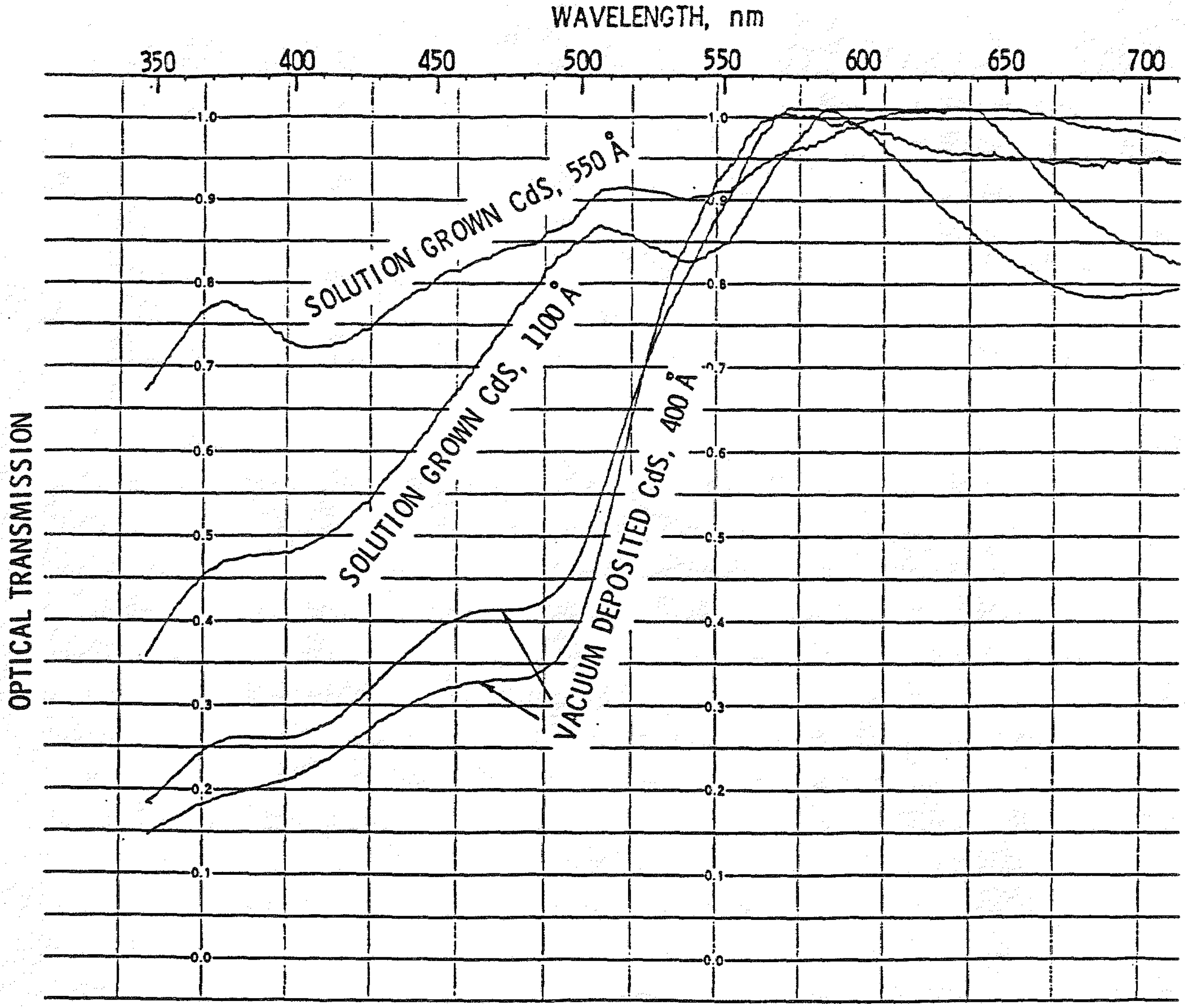


Figure 3-3 **Optical transmission spectra of CdS films deposited by solution growth and vacuum evaporation techniques.**

1000 Å thickness, and the transmission characteristics of two CdS films deposited by vacuum evaporation are also shown for comparison. The high optical transmission of solution-grown films suggests that these films are essentially stoichiometric. The vacuum evaporated films show considerably lower transmission in the above-gap region due presumably to non-stoichiometry associated with Cd inclusions. The difference in optical transmissions of two vacuum deposited CdS films of similar thickness may be related to different degree of non-stoichiometry in the films. The optical bandgap of solution grown CdS, deduced from the square absorption coefficient versus photon energy plot is 2.4-2.44 eV.

3.1.3 CRYSTALLOGRAPHIC PROPERTIES

CdS exists in two crystalline modifications: the hexagonal (wurtzite) phase and the cubic (zincblende) phase. The hexagonal phase is believed to be the stable modification between 25° and 900°C. Polycrystalline hexagonal and cubic CdS of random orientation are known to show many strong x-ray diffraction peaks, the relative intensities and the d values are summarized in Table 3-2. The crystallographic properties of solution-grown CdS films on glass and SnO_2/glass substrates and of CdS precipitates from solution were determined by the x-ray diffraction technique using CuK_α radiation. The diffraction spectra were obtained by scanning 2θ in the range of 22 - 60°. The spectra of as-precipitated CdS powder from NH_4OH-NH_4Cl solutions and the CdS powder heated at 400°C in H_2 are shown in Figure 3-4. The analysis of the spectra indicated that these samples contained both cubic and hexagonal phases with the hexagonal phase dominating. Similarly, CdS precipitates from NH_4OH - TEA solutions are predominately cubic. Most CdS films deposited on glass substrates do not show any reflections and are essentially amorphous.

Table 3.2 Powder diffraction data of hexagonal and cubic CdS using CuK_α radiation.

	Hexagonal CdS			Cubic CdS		
d	I	hkl	2θ	I	hkl	θ
3.583	75	100	24.8			
3.36	60	002	26.5	100	111	26.5
3.160	100	101	28.2			
2.90				40	200	30.8
2.450	25	102	36.6			
2.068	55	110	43.7			
2.058				80	220	43.9
1.898	40	103	47.9			
1.791	18	200	50.9			
1.761	45	112	51.9			
1.753				60	311	52.1
1.680				10	222	54.56
1.679	4	004	54.6			
1.581	8	202	58.3			
1.453				20	400	64.0
1.337				30	331	70.3

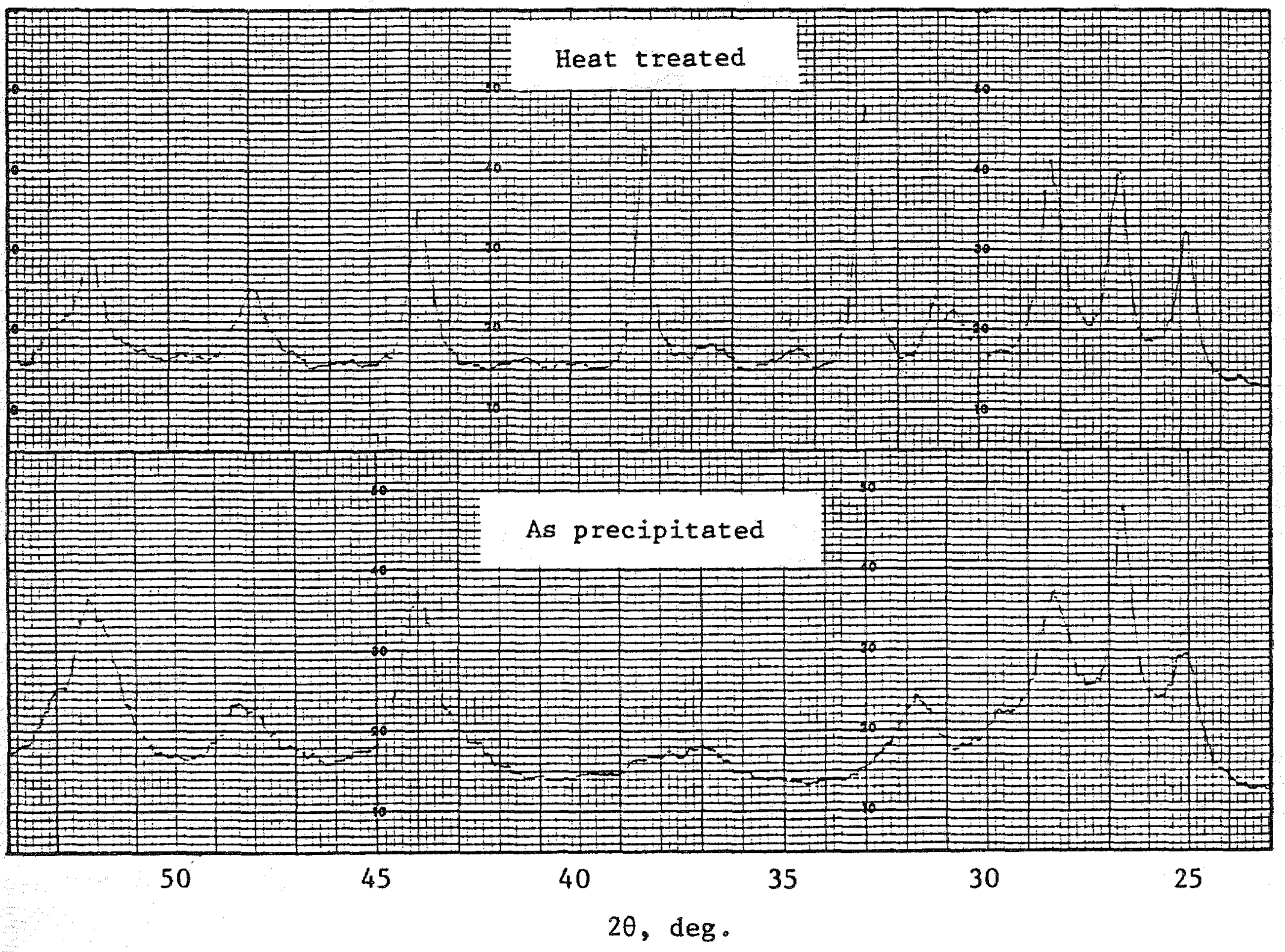


Figure 3-4 X-ray diffraction spectra of as-precipitated and heat treated CdS powder from an NH_4OH - NH_4Cl solution.

Films deposited on SnO_2/glass substrates showed considerably simpler diffraction spectra than the CdS precipitates from solution. Figure 3-5 shows the diffraction spectra of as-deposited and heat-treated (200°C and 400°C) CdS films from an NH_4OH + NH_4Ac solution. The as-deposited film shows a very strong diffraction peak at $2\theta = 26.5°$, a strong peak at $2\theta \sim 38°$, and a very week peak at $2\theta \sim 52°$. The first and third peaks are associated with both hexagonal and cubic structures, and the second peak has not been identified. Thus, the crystallographic property of the as-deposited film cannot be determined from the diffraction data measured here. After heating at 200°C for 10 min., however, one additional diffraction peak at $2\theta \sim 48°$ was observed. Since this peak is observed only in hexagonal CdS, the CdS film deposited on SnO_2/glass substrates is most likely to be of the hexagonal phase. Upon further heating at 400°C for 1 hour, only the diffraction peak at $2\theta = 26.5°$ remained, indicating that the film presumably shows a strong preferred (0001) orientation. The diffraction peak observed at $\theta \sim 38°$ may be attributed to impurities which vaporized upon heat treatment.

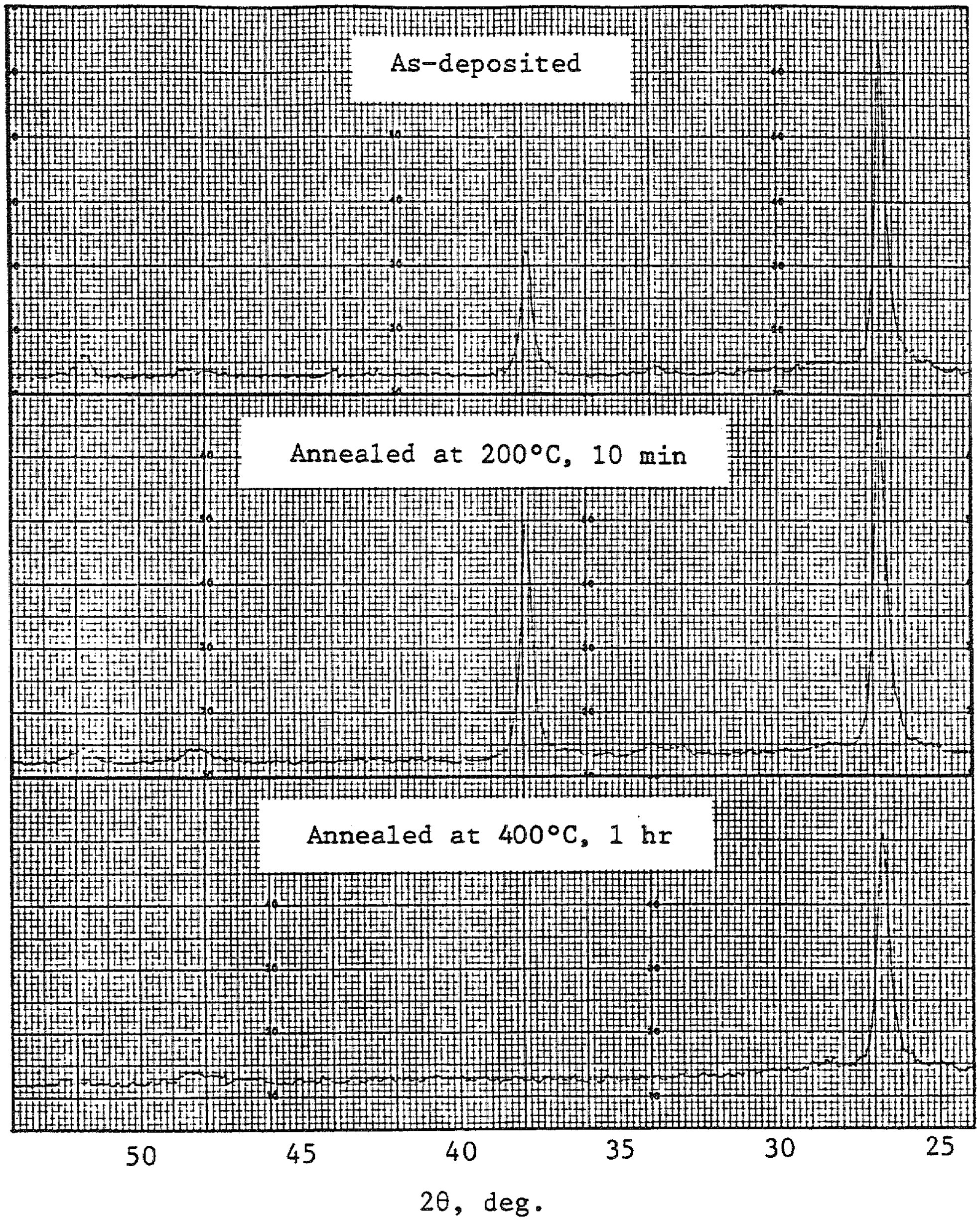


Figure 3-5 **X-ray diffraction spectra of solution grown CdS films on SnO_2/glass substrates: (a) as-deposited, (b) annealed at 200°C, and (c) annealed at 400°C.**

3.1.4 DISSOLUTION RATE

Because of the large number of process parameters affecting the properties of deposited CdS films, a simple criterion of the quality of the films has been developed. CdS is soluble in diluted hydrochloric acid, the rate of dissolution is a measure of the porosity, impurity content, and bond strain in the film and is used to evaluate the process parameters of the deposition process. An acid concentration of 0.4 M was selected on the basis of preliminary experiments.

CdS films deposited from NH_4OH + TEA and NH_4OH + NH_4Cl solutions dissolve rapidly in 0.4 M HCl, > 1000 Å/min, and these films were not further evaluated. The film deposited from NH_4OH and NH_4Cl solutions was also found to contain a high concentration of chlorine, and all solution-grown films have high concentrations of carbon and oxygen. CdS films deposited on SnO_2/glass substrates from NH_4OH + NH_4Ac solutions showed lower dissolution rates in 0.4 M HCl, about 550 Å/min for films deposited at a rate of 100 Å/min and 300 Å/min for films deposited at 40 Å/min. As a comparison, the dissolution rate of CdS films deposited by vacuum evaporation is about 1 Å/min. The high dissolution rate of solution-grown CdS is due to high porosity and high impurity content.

To minimize the effects of porosity and bond strains in solution-grown CdS films, heat treatment of these films was investigated. Most films studied were deposited on SnO_2/glass substrates from NH_4OH + NH_4Ac solutions at relatively high rates, about 100 Å/min. The selection of these films is based on the facts that CdS films deposited from NH_4OH + NH_4Ac solutions have lower dissolution rates than those from NH_4OH + NH_4Cl or NH_4OH + TEA solutions and that CdS films deposited at low rates may not be continuous. The heat treatment of CdS films was first carried out in a He atm. Partial loss of sulfur from CdS, as indicated by the increase in above-bandgap absorption, was observed at temperatures above 200°C for films heated in flowing He and at temperatures above 300°C for films heated in stationary He. The dissolution rate of CdS films was reduced from 550 Å/min to about 300 Å/min after heating in stationary He at 300°C for 2 hours. To suppress the decomposition of CdS at high temperatures, a mixture of He and H_2S was passed through the reaction tube during the heat treatment. The heating of CdS films in H_2S was found to induce recrystallization of the film, leading to discontinuities. Sulfur vapor was then used to prevent the decomposition of CdS films during the heat treatment. The dissolution rate of CdS films was reduced to about 100 Å/min after heating in a S atm at 500°C for 2 hours. This rate is about 100 times higher than the dissolution rate of CdS films deposited by vacuum evaporation, due most likely to impurities in the film.

3.1.5 THIN FILM CADMIUM TELLURIDE SOLAR CELLS

During the early stage of this program, the porosity and impurity problems associated with the solution-grown CdS films were not apparent, and as-grown CdS films deposited on SnO_2/glass substrates under a wide range of solution compositions were used for the preparation of thin film CdTe solar cells. The absorber, p-CdTe, was deposited at 600°C by the CSS technique. Ohmic contacts to p-CdTe and SnO_2 were then formed in the usual manner. In all cases, the resulting devices showed poor characteristics with low V_{oc} (<0.5V) due apparently to the chemical reactivity of solution-grown CdS associated with its porosity and contaminations.

Subsequently, densified CdS films on SnO_2/glass substrates, obtained by heating the solution-grown material in a He or S atm, were used for the deposition of p-CdTe films. Although the process parameters of the CSS process were maintained constant, the resistivity of p-CdTe films and the characteristics of the heterojunctions have not been reproducible. No meaningful correlations between the CSS parameters and properties of CdTe films and junctions can be deduced. In many cases, p-CdTe films showed high resistivities, > 1000 ohm-cm, due presumably to the doping of CdTe films by impurities in CdS. The impurity content in CdS films is probably not reproducible, and no attempts have been made to monitor the impurity content in the films. In a few instances where the process parameters of CdS deposition could have been unintentionally varied, the series resistance of the solar cell was reasonable, (3-4) ohm-cm^2. An example is shown in Figure 3-6, where the current-voltage characteristics of a solar cell of 0.47 cm^2 area, under 100 mW/cm^2 illumination with ELH lamps, are shown. The V_{oc}, J_{sc}, FF, and η are 0.74V, 19.6mA/cm^2, 0.63, and 9.2%, respectively. Further work on the improvement of the properties of solution-grown CdS films is underway.

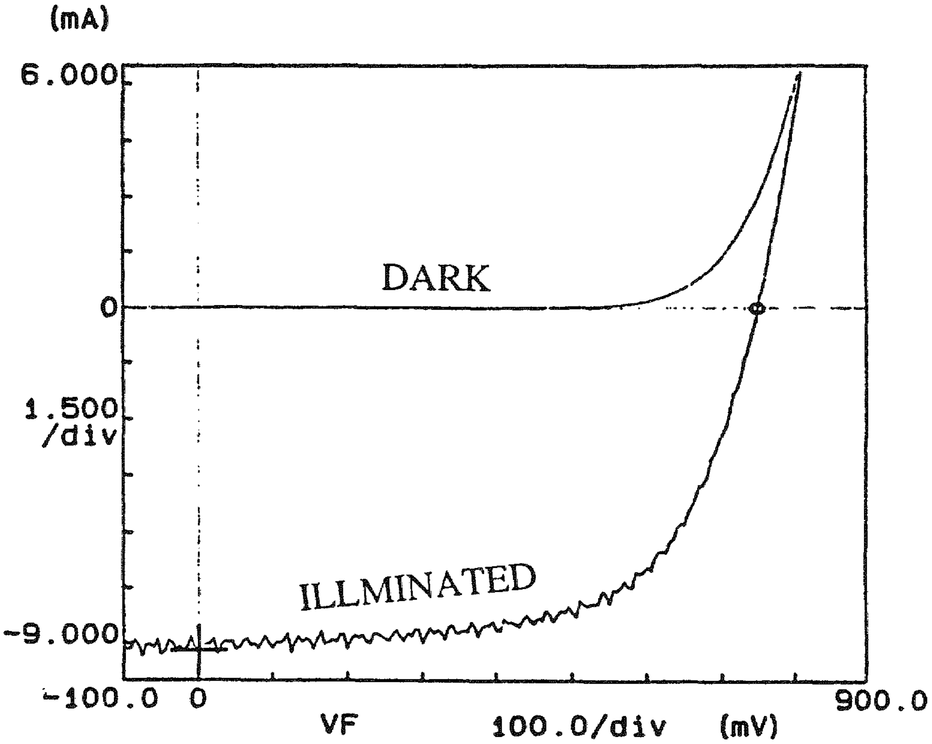


Figure 3-6 **Illuminated current-voltage characteristics of a thin film CdS/CdTe solar cell.**

3.2 ZINC OXIDE FILMS

Zinc oxide is one of the most economical TCS for applications in optoelectronic devices. Commonly used techniques for thin film deposition, such as sputtering, spraying, CVD, etc., have been used in the deposition of ZnO films. The growth of ZnO films from aqueous solution has also been reported recently [13]. In this technique, solutions of a zinc salt, a freezing agent (NH_4F), and a catalyst ($AgNO_3$) were placed in a beaker containing vertically suspended substrates. A NaOH solution was added to deposit zinc hydroxide on the substrate surface. By heating the hydroxide films at 180° - 200°C for 2-3 hours, zinc oxide films were obtained. A number of deposition experiments were carried out using similar procedures. Since the nucleation of zinc hydroxide on glass substrates is difficult, the majority of the deposition experiments was carried out using SnO_2/glass substrates. Films greater than about 2000 Å in thickness are milky in appearance and show poor transmission in the visible region, due presumably to contamination. The incorporation of dopants into ZnO films also appears to be erratic. Since the results in Ref 13 cannot be readily reproduced, the solution growth of ZnO films was not pursued further.

The deposition of ZnO films by MOCVD has been reported [14]. The oxidation of DMZn with oxygen in the substrate surface in a He flow was investigated in this program. Using DMZn at a partial pressure of 0.2-0.4 Torr and an O_2/DMZn molar ratio of 20-40, ZnO films were deposited on glass or SnO_2/glass substrates at 200°-250°C at 0.5-1 μm/hr. The low deposition rate was used to minimize the gas phase reaction. Preliminary measurements indicate that the MOCVD films have an optical bandgap of 3.35-3.45 eV and a room temperature resistivity of 60-300 ohm-cm.

3.3 ZINC SULFIDE FILMS

The MOCVD technique was also used for the deposition of ZnS films. Using DMZn at a partial pressure of 0.2-0.4 Torr and a H_2S/DMZn ratio of 10-20, ZnS was deposited on the surface of glass or SnO_2/glass substrates at 350°C in a H_2 flow. The deposition rate was also low, about 1 μm/hr, in order to minimize gas phase reactions. The deposited films are highly transparent in the visible region and have electrical resistivities in the range of 100-500 ohm-cm.

SECTION 4.0

ZINC TELLURIDE FILMS AND HETEROJUNCTIONS

Thin film CdTe heterojunction solar cells have been under development for over forty years, and steady progress has improved the conversion efficiency to over 11%. Continued optimization of the process parameters will increase the efficiency to 15 - 17% range, which is limited by the interface recombination, the inefficient use of the solar spectrum, and other losses. If two solar cells of direct gap semiconductors with appropriate bandgap energies are used in tandem, the overall conversion efficiency can be improved significantly. Two solar cells can be connected to form a two-terminal or four-terminal device. The four-terminal devices are most practical, since two separate external circuit loads are used and the photocurrents through each cell do not have to be the same. Thus, the match in thermal expansion coefficients of the two semiconductors and the formation of tunnel junctions, required in two-terminal devices, are not necessary. Consequently, a much larger selection of semiconductors is possible. The maximum conversion efficiency of four-terminal, single-crystalline cell tandem structures have been calculated to be 36.6% at AM 1.5. Efficiencies of 20% - 25% can be expected from polycrystalline thin film four-terminal two-cell structures. The optimum bandgap energies for the upper and lower cells are 1.7 -1.9 eV and 1.0 - 1.1 eV, respectively. The $CdZnS/CuInSe_2$ heterojunction cell (bandgap energy of $CuInSe_2$: 1.0 eV) is a promising candidate for the lower cell. The upper cell may be prepared from a number of solid solutions. For example, HgTe (a semimetal) and ZnTe (Eg = 2.25 eV at 300K) form a continuous series of solid solutions, and the solid solution of the composition $Hg_{0.3}Zn_{0.7}Te$ has a room temperature bandgap of about 1.7 eV. Preliminary to the investigation of $Hg_{1-x}Zn_xTe$ films, the deposition and characterization of ZnTe films have been carried out.

Zinc telluride with a room temperature bandgap energy of 2.25 eV is not an ideal absorber of the top cell in a cascade structure. However, the simplicity of the fabrication of thin film ZnTe cells, such as the ZnO/ZnTe structure, could be most economical when used in conjunction with the $CuInSe_2$ cell. Zinc telluride crystallizes in the zincblende structure with a lattice parameter of 6.104 Å. Most work on zinc telluride has been concerned with single crystalline material for optoelectronic applications. ZnTe crystals are usually of p-type conductivity due to self compensation by native defects. Copper and silver introduces shallow acceptors at 149 and 124 meV, respectively. Copper, the most important residual impurity in ZnTe, has a high diffusion coefficient and is almost unavoidable in bulk crystals. ZnTe is more stable than CdTe; the equilibrium vapor pressure of Te_2 from ZnTe is negligible at 500°C, as shown in Figure 4-1, where the equilibrium vapor pressure of Zn and Te_2 are also shown for comparison.

4.1 THE DEPOSITION PROCESS

The deposition of ZnTe films on glass and coated-glass substrates (SnO_2/glass, ZnO/SnO_2/glass, and ZnS/SnO_2/glass) has been carried out by the reaction of DEZn and DETe in a hydrogen atmosphere. The apparatus used for the deposition of ZnTe films is similar to that for the deposition of CdTe films (Figure 2-4). The process parameters, substrate temperature and reaction mixture composition, were adjusted so that SnO_2/glass, ZnO/SnO_2/glass, and ZnS/SnO_2/glass substrates were

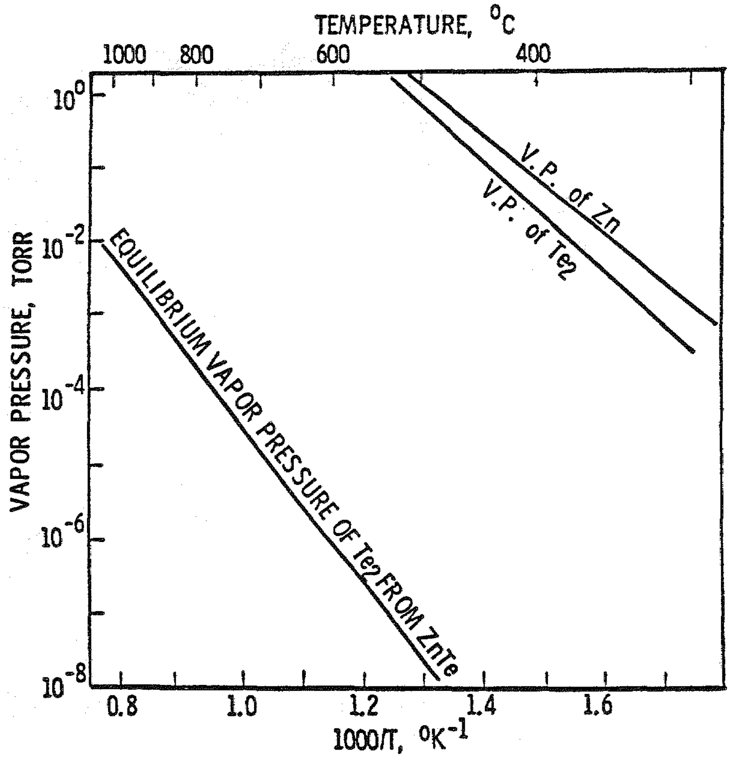


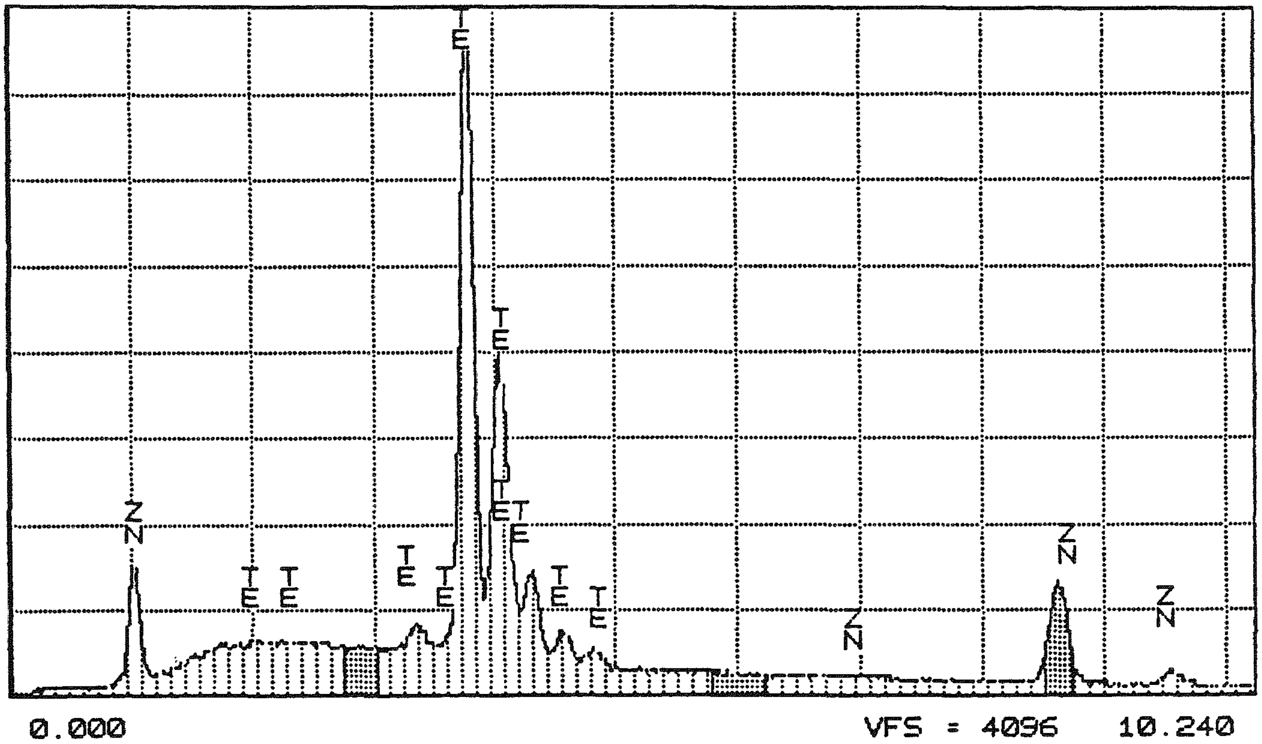
Figure 4-1 **Equilibrium vapor pressure of Te_2 from the dissociation of ZnTe and the equilibrium vapor pressures of Zn and Te_2.**

not affected by the H_2 atm and that the formation of ZnTe occurred predominately on the substrate surface.

A number of ZnTe films were deposited at 370° - 380°C using hydrogen containing 0.1 to 0.2 Torr of organometallic at a flow rate of 2 ℓ/min. The DEZn/DETe molar ratio in the reaction mixture was 0.8 - 1.3. The deposition rate of ZnTe was 2-3 μm/hr, depending on the composition of the reaction mixture.

4.2 PROPERTIES

The ZnTe films deposited by MOCVD are adherent to the substrates and are essentially stoichiometric. The typical results of the electron microprobe analysis of a ZnTe film on a glass substrate are shown in Figure 4-2. The crystallographic properties of ZnTe film were determined by the x-ray diffraction technique using CuK_α radiation. Polycrystalline ZnTe powder of random orientations is known to show a number of diffraction peaks, as summarized in Table 4-1. The diffraction spectra of ZnTe films were obtained by scanning 2θ in the range of 20° - 60°. A typical spectrum is shown in Figure 4-3, where all strong diffraction peaks are present, and the film is essentially polycrystalline.



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----     K       [Z]     [A]     [F]    [ZAF]  ATOM.%  WT.%
TE-L   0.616   1.069   1.007   0.998   1.075   49.27   65.66
ZN-K   0.384   0.884   1.019   1.000   0.901   50.73   34.34
```

Figure 4-2 Electron microprobe analysis of a MOCVD ZnTe film.

Table 4-1 Powder diffraction data of ZnTe

d	hkl	I/I_o
3.523	111	100
3.051	200	10
2.159	220	80
1.840	311	35
1.762	222	4
1.526	400	8
1.4003	331	14
1.3645	420	4
1.2456	422	10

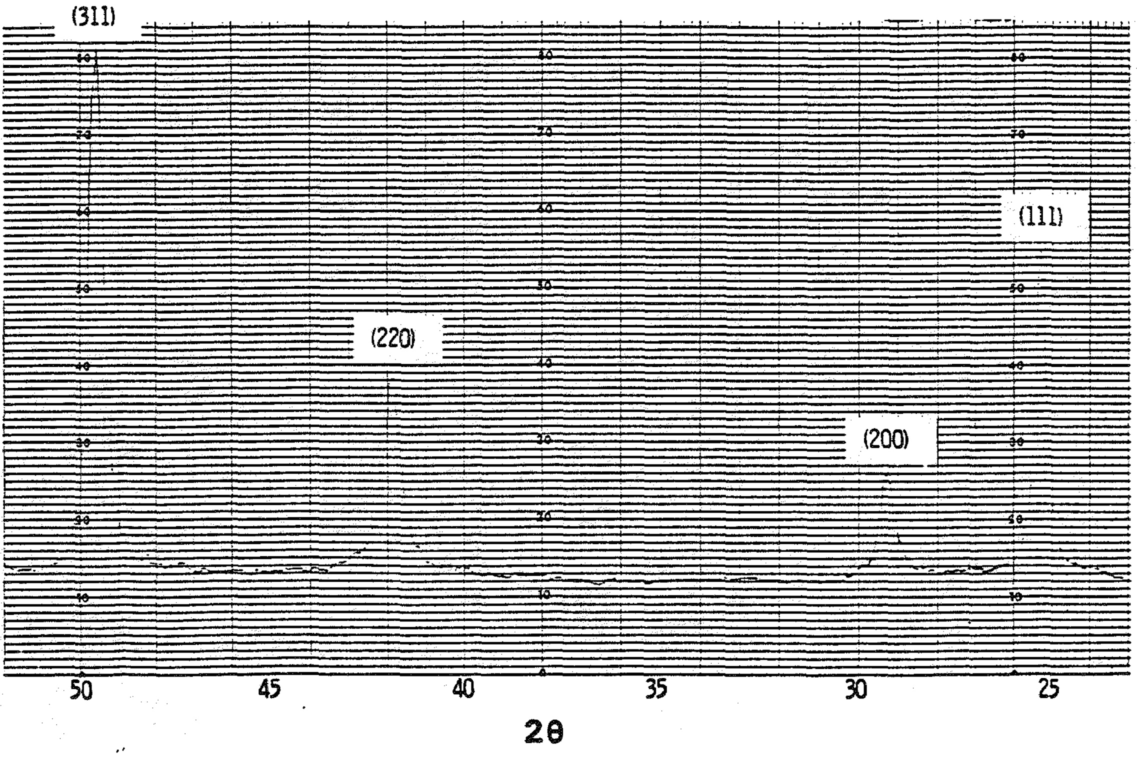

Figure 4-3 X-ray diffraction spectrum of a MOCVD ZnTe film.

The optical absorption of ZnTe films deposited on glass substrates was measured. Figure 4-4 shows a α^2 versus E plot, yielding an optical bandgap of 2.2 eV.

The MOCVD ZnTe films deposited on glass substrates are all p-type. Low resistance ohmic contacts were made to ZnTe films by electroless Au deposited from a $AuCl_3$ solution; however, these contacts usually penetrate the entire thickness of the film. The resistivity of ZnTe films was measured by the conventional potential probe technique. The variation of resistivity with the composition of the reaction mixture is shown in Figure 4-5, where a minimum, about 1000 ohm-cm, occurs at a DeZn/DETe molar ratio of about 1.15. This resistivity is presumably the minimum obtainable by intrinsic doping at 370° - 380°C. It is probably difficult to incorporate dopants, such as P or As, into ZnTe films because of the thermal stability of the dopant compounds.

Heterojunctions were prepared by depositing ZnTe films on TCS coated glass substrates, such as SnO_2/glass, ZnO/SnO_2/glass, and ZnS/SnO_2/glass, at 370° - 380°C in a H_2 atm. The formation of a low resistance contact to ZnTe film in the heterojunction structure was found to be difficult. Although electroless Au makes a low resistance contact to ZnTe films on glass substrates, it is unsuitable for ZnTe/TCS heterojunctions because of the penetration of the $AuCl_3$ solution through the ZnTe film. Copper or silver films deposited on ZnTe films by vacuum evaporation were not adherent even after annealing. The use of graphite paste, Cu-doped graphite, and Au-doped graphite paste as ohmic contact to ZnTe was investigated. The contact resistance was reduced by heat treatment

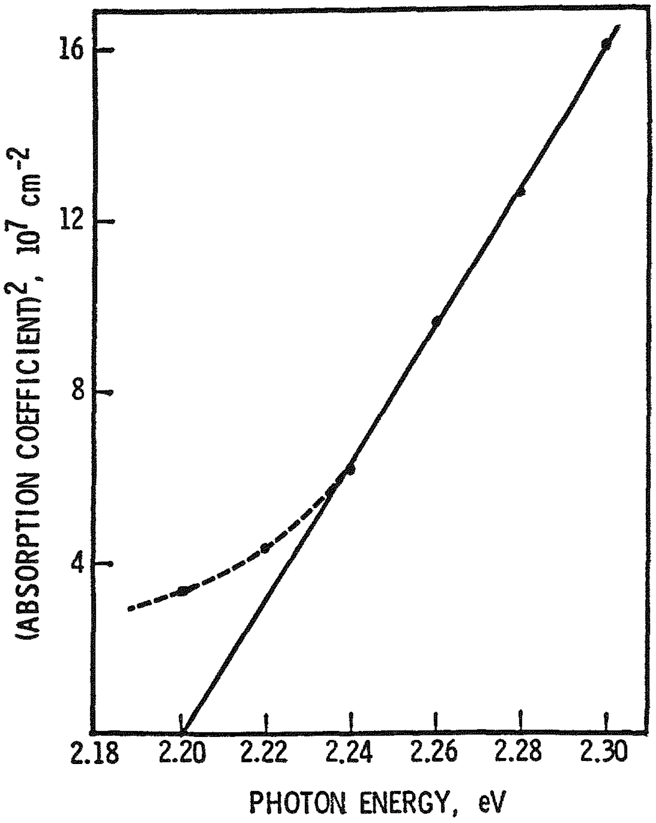

Figure 4-4 Optical absorption data of a ZnTe Film

at 250°C in all cases; however, current-voltage measurements indicated that the doped graphite contacts had higher contact resistance. The accurate determination of the contact resistance between graphite and ZnTe is difficult because of the high sheet resistance of ZnTe films. Preliminary results indicated that under 100 mW/cm^2 illumination with ELH lamps, ZnS/ZnTe junctions had open-circuit voltages of 0.6 - 0.7 V as compared with 0.1 - 0.2V for ZnO/ZnTe junctions. Photocurrents were low in both cases because of the high contact resistance between graphite and ZnTe.

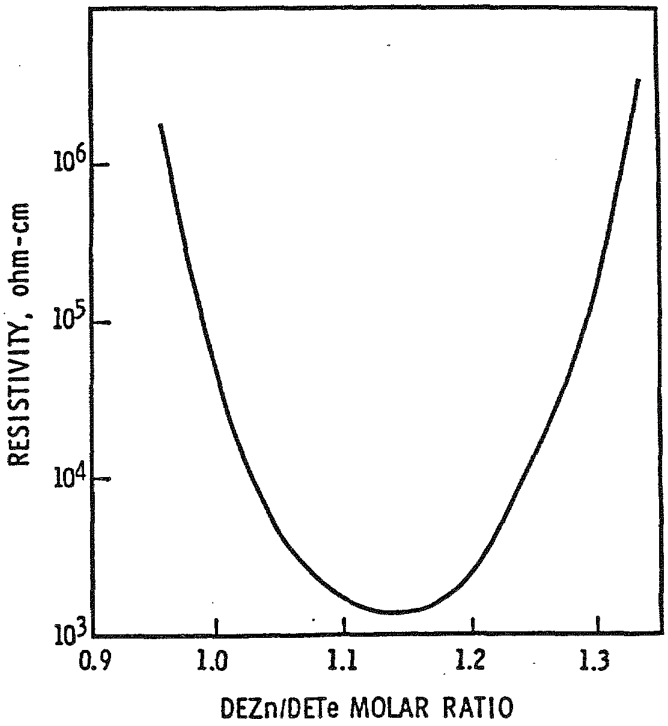

Figure 4-5 Resistivity of MOCVD ZnTe film as a function of reactant composition.

SECTION 5.0

CONCLUSIONS

- Solution growth is a low cost technique for the deposition of CdS films. The solution-grown CdS films show good optical transmission in the above-bandgap region; however, they are porous and impure. While these films can be densified by heat treatment, impurities cannot be readily removed.

- Thin film CdS/CdTe solar cells prepared from solution-grown CdS films show inferior characteristics as compared to those from vacuum evaporated CdS films.

- MOCVD has been shown to be a flexible low temperature technique to control the conductivity type of, and, to a limited extent, carrier concentration in CdTe films. Thin film CdTe homojunctions can thus be prepared by varying the composition of the reaction mixture during the deposition process.

- MOCVD is well-suited for the deposition of ZnO and ZnS films at relatively low temperatures.

- The successive in-situ deposition of ZnS and ZnTe films on SnO_2/glass substrates is a promising technique for the preparation of ZnS/ZnTe heterojunctions.

SECTION 6.0

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