

25
20-86. JT (1)

(30)
I, 27608

DR-1892-9

SERI/STR-211-2972
DE86010720

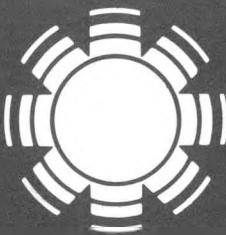
June 1986

Tandem Thin-Film Solar Cell Using $\text{Cd}_y\text{Zn}_{1-y}\text{Te}$ as the Wide Bandgap Component

Annual Subcontract Report
1 April 1985 - 1 April 1986

K. Zanlo
Ford Aerospace and
Communications Corporation
Newport Beach, CA

Prepared under Subcontract No. XL-5-04074-08



SERI

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401-3393

Operated for the
U.S. Department of Energy
under Contract No. DE-AC02-83CH10093

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SERI/STR-211-2972
UC Category: 63
DE86010720

SERI/STR--211-2972

DE86 010720

Tandem Thin-Film Solar Cell Using $\text{Cd}_y\text{Zn}_{1-y}\text{Te}$ as the Wide Bandgap Component

Annual Subcontract Report
1 April 1985 - 1 April 1986

K. Zanio
Ford Aerospace and
Communications Corporation
Newport Beach, CA

June 1986

SERI Technical Monitor:
R. Mitchell

Prepared under Subcontract No. XL-5-04074-08

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401-3393

Prepared for the
U.S. Department of Energy
Contract No. DE-AC02-83CH10093

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 

ABSTRACT

The objective of this program is to develop CdZnTe as the wide bandgap component for an all thin-film polycrystalline tandem solar cell. Single crystal and polycrystalline CdZnTe films containing about 0.20 mole fraction of ZnTe corresponding to a bandgap of 1.65 eV were deposited by congruent evaporation in UHV on sapphire and ITO/GLASS substrates. CdZnTe and single crystal CdTe films, semi-insulating as grown films, were annealed to p-type in Te overpressures. The Hall mobilities and carrier concentration ranges for the films were respectively 20-75 cm²/Vsec and $5 \times 10^{14} - 10^{16}$ cm⁻³. The use of Hg(Cd,Zn) Te alloys reduced contact resistances as low as 0.1 ohm-cm². Indium Schottky barriers of 0.9 eV were observed on CdZnTe single crystal thin films.

Blank Page

PREFACE

This report describes the preparation of CdZnTe thin films by congruent evaporation in UHV on ITO/GLASS and sapphire substrates. The motivation for preparing CdZnTe films is to develop a wideband gap absorber for an all thin film tandem solar cell. The evaluation of the absorber, by Hall, optical, x-ray, and Schottky barrier measurements is also described. This report also describes the formation of Hg(CdZn) Te alloys by vapor transport and subsequent interdiffusion. The motivation of preparing these alloys with Hg is to make ohmic contact to the p-type absorber layers.

The principal investigator is Dr. Kenneth Zanio. Program Manager is John Roschen. Ken Hay is responsible for the preparation of the CdZnTe film, Dr. Robert Kay is responsible for the preparation of the CdHgTe film and Dr. Ross Bean is responsible for the preparation and characterization of the substrate. Yvonne McNeil and Margaret McNally provided technical assistance. Work was performed in the Detector Development Section of the Semiconductor Technology Department.

SUMMARY

OBJECTIVE

The highest efficiency of a single junction all thin film polycrystalline solar cells is presently about 11 percent. A tandem cell having bandgaps of about 1.0 eV and 1.65 eV has the potential of extending this efficiency^{1,2,3} to 15 percent. The leading candidate⁴ for the narrow bandgap cell is CuInSe₂ which has a bandgap of about 1.0 eV and an efficiency of about 11 percent. The broad objective of this effort is to develop an efficient wide bandgap cell. We are exploiting alloys of CdTe to achieve this goal.

One of the alloys which will extend the bandgap of CdTe to 1.65 eV is Cd_yZn_{1-y}Te. CdTe and ZnTe are completely miscible⁵ in the liquid and solid phases for all y. Bulk single crystal n and p-type Cd_yZn_{1-y}Te has been prepared over a wide range^{6,7} of y. The first goal of this program is to prepare thin films of Cd_yZn_{1-y}Te by a practical deposition technique that also results in an absorber layer of acceptable crystallinity and optical and electrical quality. The second goal is to make both ohmic and transparent contact to the absorber layer. The third goal of this program is to demonstrate that our approach could lead to a practical wideband gap component for an all thin film tandem solar cell.

DISCUSSION

Our concept of a practical tandem polycrystalline thin film solar cell is shown in Figure 1 (Left). Both the narrow bandgap and wide bandgap cells are prepared on rigid substrates and sandwiched together to form the tandem cell. The leading narrow bandgap candidate is CuInSe₂. The wider bandgap cell consists of a p-type Cd_yZn_{1-y}Te thin film on a recrystallized (RX) CdS/ITO/Glass substrate. In this program, we have prepared single crystal and polycrystalline CdZnTe films on sapphire and ITO/Glass substrates by congruent evaporation in ultra high vacuum. To separate out conflicting effects from the grain boundaries, we initially concentrated on the preparation of single crystal Cd_yZn_{1-y}Te thin films for a test cell (Right). Thin films of CdTe and their ZnTe alloys are semi-insulating as grown. Intentional annealing in Te over-pressures lowers their resistivity and results p-type material. Our p-type CdTe thin films have mobilities comparable to those for bulk CdTe.

One of the major obstacles to making a practical CdZnTe solar cell is the difficulty in making both transparent and ohmic contact to p-type CdZnTe. The approach here is to make ohmic and transparent contact through an intermediate p-type ZnTe thin film. Before we can make adequate contact to the ZnTe thin film we established that we could make ohmic contact to p-type CdTe and CdZnTe. Au is one metal which has been used with limited success to contact p-type CdTe. We have found that intermediate layer of p-CdHgTe between the metal contact and the CdTe and an intermediate layer of CdZnHgTe between the metal contact and the CdZnTe both enhance ohmic behavior. The effect of the intermediate Hg-rich layer is to allow Au to make p+ contact to CdTe since p-CdHgTe and p-CdTe should all be nearly ohmic by the common position of the valence band. For the same reason, improved ohmic contact has been made to p-CdZnTe and could be made to p-ZnTe since they also contain the common anion^{8,9} Te.

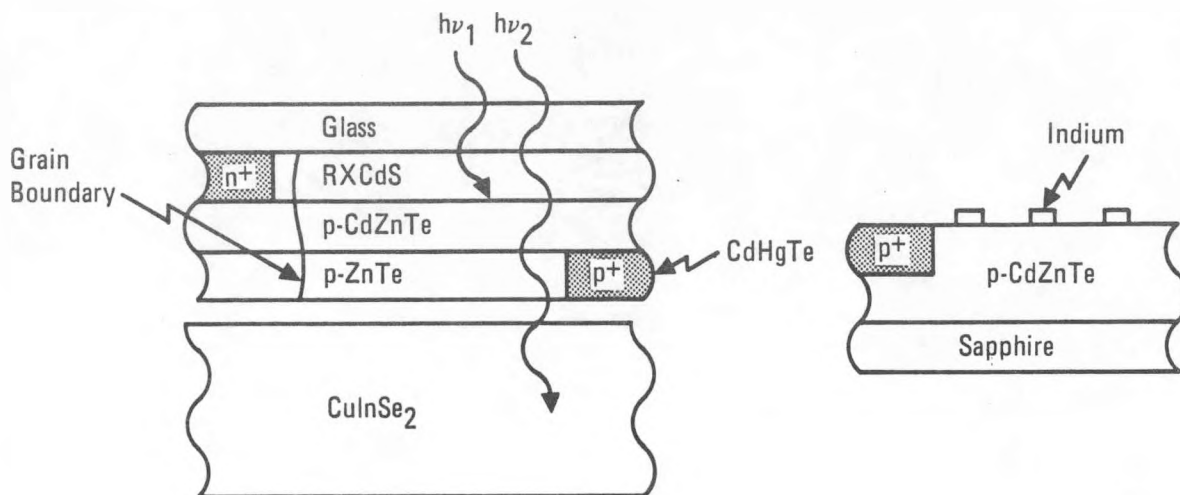


FIGURE 1. (Left) A Practical Multilayer Narrow Bandgap and Wide Bandgap Tandem Polycrystalline Thin Film Solar Cell and (Right) the Wide Band Gap Single Crystal Test Structure Utilized in This Program

Test structures were made with the CdZnTe films on sapphire. Both single crystal and polycrystalline devices showed diode characteristics with preliminary barrier heights of respectively 0.9 eV and 0.5 eV.

CONCLUSIONS

The results from this program are favorable for developing CdZnTe as the wide band component in an all thin film tandem solar cell. P-type films of CdZnTe with an optical band gap of about 1.65 eV have been prepared. Improved ohmic contact to p-type CdTe and p-CdZnTe has been demonstrated. Preliminary device results from single crystal and polycrystalline p-type CdZnTe on sapphire are encouraging.

CONTENTS

	PAGE
PREFACE	iii
SUMMARY	iv
CONTENTS	vi
ILLUSTRATIONS	vii
TECHNICAL DISCUSSION	1-1
1.0 THE ULTRA HIGH VACUUM GROWTH SYSTEM	1-1
2.0 ABSORBER LAYERS	2-1
2.1 Growth of Absorber Layers	2-1
2.2 Annealing of Absorber Layers	2-5
3.0 P ⁺ CONTACTS WITH Hg-ALLOYING	3-1
3.1 HgCdTe on Single Crystal CdTe Substrates	3-1
3.2 Hg-Alloys on CdZnTe Thin Films	3-2
3.3 Interdiffusion	3-3
4.0 TRANSPARENT p-TYPE WINDOWS	4-1
5.0 CdZnTe DEVICES	5-1
6.0 PLANS	6-1
REFERENCES	R-1

ILLUSTRATIONS

FIGURE		PAGE
1	(Left) A Practical Multilayer Narrow Bandgap and Wide Bandgap Tandem Polycrystalline Thin Film Solar Cell and (Right) the Wide Band Gap Single Crystal Test Structure Utilized in This Program	v
2	(Top) Schematic and (Bottom) Photograph of Source and Carousel Substrate in UHV CdZnTe Growth System	1-2
3	Selected Area Electron Channelling Patterns of CdTe and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ Thin Films on (0001) Sapphire	2-2
4	Optical Bandgap vs Composition for $\text{Cd}_y\text{Zn}_{1-y}\text{Te}$	2-4
5	(a) Ampoule and (b) Enlargement of Source/Substrate Chamber for the Growth of CdHgTe by the Closed-Space Vapor Phase Exptaxy (CSVPE) Technique	3-1
6	I vs V Characteristics for Au/CdTe and Au/CdHgTe/CdTe Structures .	3-2
7	Formation of HgCdZnTe Contacts on CdZnTe Films by (Top) Selective Removal of SiO_2 Cap and Subsequent HgCdZnTe Growth and (Bottom) Growth and Selective Removal of HgCdZnTe Film	3-3
8	The Interdiffusion Coefficient for HgTe ($x = 0$) and CdTe ($x = 1$) .	3-4
9	Cd Microprobe Data for $\text{Cd}_{0.36}\text{Hg}_{0.64}\text{Te}$ Deposited on CdTe by Closed Space Vapor Deposition at 525°C	3-5
10	Transmission Spectrum for ZnTe Thin Film Prepared by Congruent Evaporation	4-1
11	I vs V Characteristics for Indium Schottky Barriers on (top) Single Crystal and (bottom) Polycrystalline CdZnTe Thin Films Having 20 Percent Mole Fraction of ZnTe.	5-1

TECHNICAL DISCUSSION

1.0 THE ULTRA HIGH VACUUM GROWTH SYSTEM

In an effort supported by internal research funds we have developed an Ultra High Vacuum carousel system for depositing II-VI compounds and their alloys on 2" diameter substrates. The system utilizes a mechanical blower to reach 100 torr, a dual stage sorption pump to reach 10^{-2} torr and an 8-port differential ion pump to reach the ultimate base pressures in the low 10^{-9} torr range. A titanium sublimator with a liquid nitrogen jacket are used to maximize pumping speed. A 17-inch bell jar houses the deposition chamber.

Films were grown on ITO/Glass and sapphire substrates. Substrates were prepared for depositions in Class 100 hoods in a class 1000 clean room. The ITO/Glass substrates from Donnelly Mirror were degreased and blown dry in methanol and DI. The sapphire substrates were degreased with a hot solvent spray, an HF and HCl acid, and an NH_3OH rinse to further remove organics and other particulates on the surface. The sapphire substrates were mounted in a molybdenum heater assembly Figure 2, which is capable of heating the substrates to an annealing temperature of 925°C . After mounting the substrates in the heater assembly, the chamber is then pumped down to 10^{-8} torr. Base pressures of less than about 10^{-7} torr are required to obtain single crystal films on sapphire. Higher residual pressures may either interfere with the reconstruction process occurring on the sapphire surface during the 975° anneal or coat the sapphire with an unwanted film. As discussed in the next section the electrical properties of the films are presently dominated by deviations from stoichiometry rather than by impurities introduced from residual gases.

The carousel system has the capacity for handling four 2" diameter substrates. Position 1 is for wafer mounting. Position 2 is for annealing. Separate sources are located at positions 3 and 4 for depositing films of a different composition. Quartz lamp heaters heat the substrates by radiation to about 300°C during deposition.

Radak II heaters with a 1 inch aperture are used to sublime the CdTe and CdZnTe. A UTI mass spectrometer is available to monitor residual gasses during deposition. The procedure for growth is as follows: The source material is outgassed at 580°C for 10 minutes. The source is then allowed to cool to 530°C while the substrate is cooled to about 320°C . When these temperatures are reached, the shutter is opened to begin the deposition. Typical growth rates are about 1.5 microns per hour.

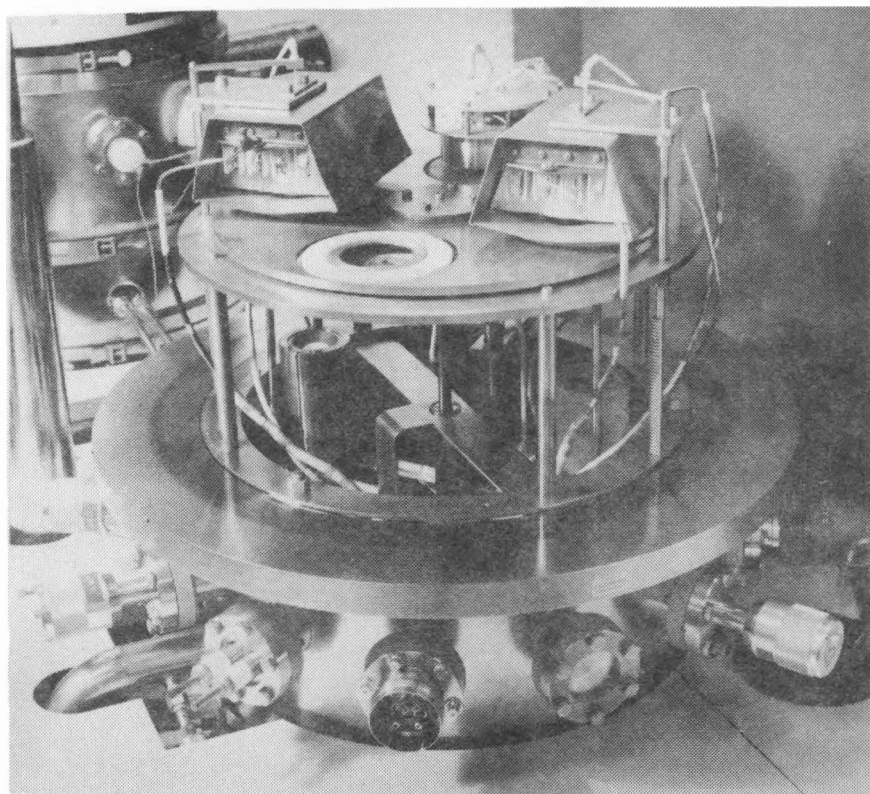
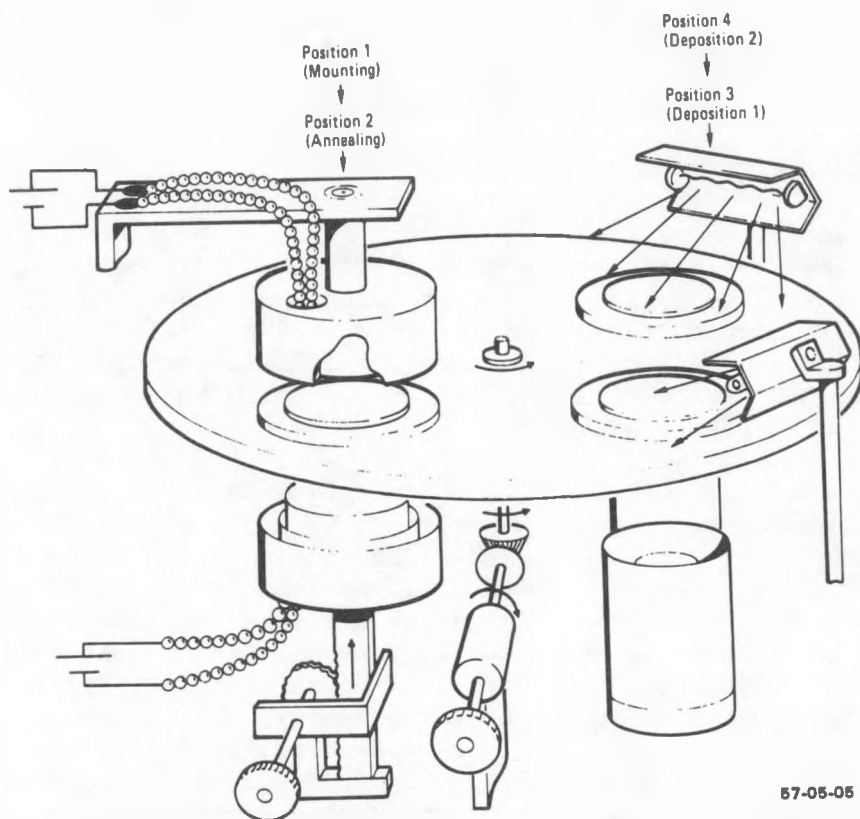


FIGURE 2. (Top) Schematic and (Bottom) Photograph of Source and Carousel Substrate in UHV CdZnTe Growth System

2.0 ABSORBER LAYERS

2.1 Growth of Absorber Layers

2.1.1 CdTe

The system has been primarily used to grow CdTe on sapphire as a subsequent substrate for HgCdTe¹⁰. However, the growth of CdTe on sapphire has been useful to this program for several reasons. First the use of a semi-insulating substrate allows a straightforward measurement of the electrical properties of the film. Second the growth of single crystal thin films allows ambiguous effects from grain boundaries to be separated out. Third the quality of the CdTe film serves as a check on the growth conditions for CdZnTe films.

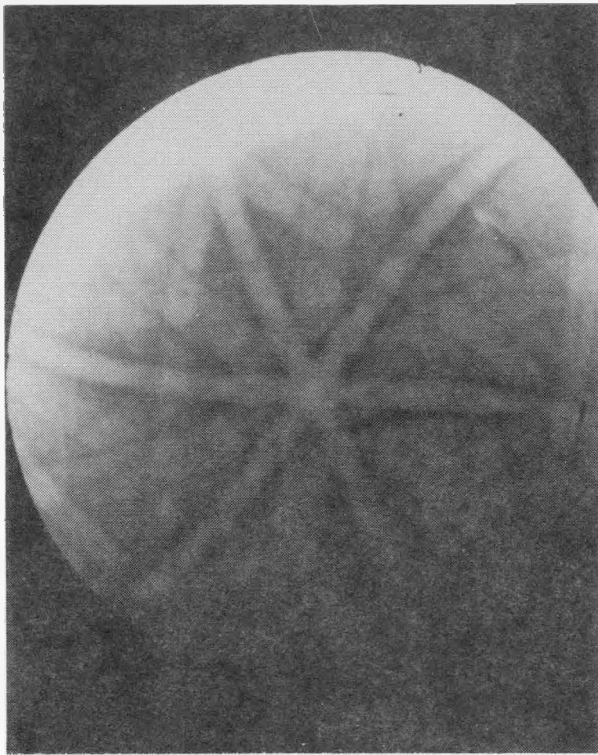
Two inch diameter epitaxial films of CdTe have been grown on (0001) sapphire. Films are of uniform thickness (± 0.5 microns) and have a uniform structural quality. Double crystal x-ray rocking curve measurements at nine positions on our best 2 micron thick film a separate internal program varied from 3 to 5 arc minutes (FWHM). Since this film was only 2 microns thick the x-ray beam penetrates into the misfit dislocation region near the sapphire/CdTe interface. The reflected beam averages the higher quality surface with the lower quality interfacial region. Based upon the evaluation of different thickness films on smaller diameter sapphire substrates, the quality of the film at the surface is estimated to be as low as 2 arc minutes.

For this program we grew a 2.0 micron thick (111) CdTe film on a 2" diameter sapphire substrate. X-ray rocking curve measurement showed it had a FWHM of 7 arc minutes. A corresponding selected areas electron channelling diffraction (SACP) pattern is shown in Figure 3A. The field of view shown in the accompanying photographs samples about a fifty micron diameter of the thin film surface. This pattern was typical of the film on the entire two inch diameter sapphire wafer. The CdTe/sapphire structure was diced up into 1/4 inch by 1/4 inch samples for a variety of experiments.

2.1.2 CdZnTe

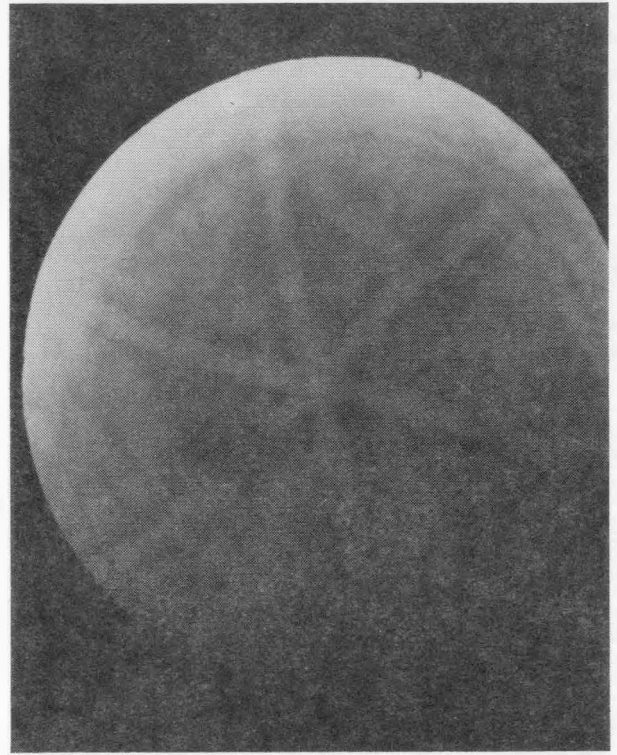
2.1.2.1 Composition Control. The control of the Cd/Zn ratio is important to the development of the CdZnTe cell. It is necessary that source material of a specified composition is readily available. It is also important that the source conditions are relatively reproducible so that when the source is replaced with material of the same composition the film composition remains the same.

Source material for this program was obtained from a CdZnTe boule grown from the melt by the Bridgman technique. Source material with the same Cd/Zn ratio was not available from all sections of the CdZnTe boule because the segregation coefficient¹¹ for Zn in CdTe is about 3. Consequently material from the nose section of a boule had a higher Zn content than material from the tail of a boule. For this program we used a one and one half inch diameter 2 inch long boule from the Fermionics Corporation which had a Zn concentration of 22 atomic percent near the nose but only a 10 atomic percent at the tail. To a lesser extent radial distribution in Zn content can also be expected. Therefore it is possible to obtain



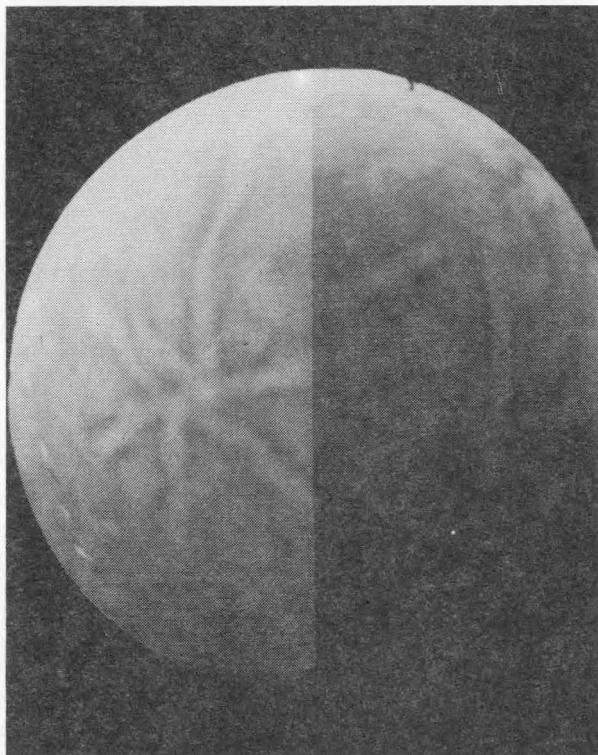
Single Crystal CdTe

A



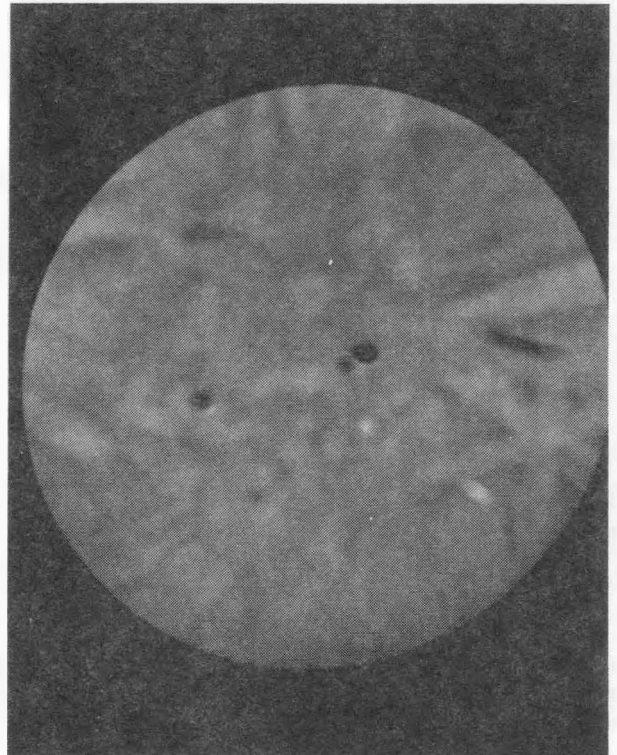
Single Crystal $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$

B



Single Crystal $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$

C



Polycrystalline $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$

D

FIGURE 3. Selected Area Electron Channelling Patterns of CdTe and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ Thin Films on (0001) Sapphire

source material, but this material will have composition gradients. Our present supply of source material is adequate for these studies. However, an alternate supply of source material is needed for more precise work and when a higher throughput of thin films is required.

In the first quarter we used source material with a y -value of 0.809. This material was from a different boule grown at an earlier date. We obtained films with a y value of 0.796. A band gap of 1.63 eV was obtained from transmission measurements. We consumed that source material in first quarter. In subsequent studies we used the wafer near the nose of the Fermionics boule which had a y of 0.78. The corresponding band gap from transmission measurements was 1.58 eV. We grew films with a band gap of 1.59 eV. A general observation is that Zn content in the film is slightly higher than that of the source. Results this quarter also further confirm that the band gap is less than expected from a linear extrapolation of the y -value. More accurate EDAX and transmission measurement are needed to determine the actual sublinear relationship on Figure 4.

2.1.2.2 Control of CdZnTe Crystal Quality. Best device performance is expected for a single crystal device. A practical all thin film cell will be polycrystalline due to the requirement of a low cost substrate. The quality of the crystal within the grain boundaries of the all thin film will influence device performance. We are attempting to prepare polycrystalline CdZnTe with an intragrain quality comparable to single crystal films. We achieve this as we are growing single crystal and polycrystalline CdZnTe films under growth conditions as similar as possible. Our approach has been to first establish the conditions for single crystal growth and then grow polycrystalline film with a slight change in single crystal growth conditions. For example, either a small increase in the growth rate or decrease in the substrate temperature might initiate polycrystalline growth.

Using a composite substrate consisting of a few thousand Angstroms of single crystal CdTe on sapphire we grew single crystal CdZnTe about 5 microns thick at a growth rate of 1 micron/hr. An increase in the growth rate to 6 microns/hr also resulted in single crystal material. Lowering the substrate temperature about 25°C at this increased growth rate resulted in polycrystalline films.

Figure 3B shows the typical SACP pattern of a 5 micron thick single crystal $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ film. The quality of these patterns were only fair and sensitive to position. It is possible that the surface contains a thin overlay of contaminants. If not, the quality of the SACP pattern corresponds to a FWHM from 8 to 20 arc minutes for the x-ray rocking curves. Figure 3C shows the channelling patterns of a six micron thick $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ film grown at the higher growth rate of 6 microns/hr. The base (111) pattern was easily discerned across the surface. However, the position of the (111) node (spoke center) was extremely sensitive to position. This indicates a multigrain structure with (111) plane tilts varying as much as 8 degrees. The interruption of a single pattern within a single field of view indicates multiple grains or subgrains within the approximately 50 micron field of view. The abrupt change in density in this Figure is due to charging and is discussed below. Figure 3D shows diffraction patterns of a polycrystalline $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ film grown at the same 6 micron/hr growth rate but at a lower substrate temperature. These images were also characteristic of the entire two inch diameter film. Separate small areas of (111) patterns were evident in the same field of view, characteristic of separate grains. As the SACP pattern samples a region of about 50 microns, this is a reasonable order of magnitude estimate of the grain size.

SAMPLE	SYMBOL	y	E _g (eV)
CdTe FILM	□	1.0	1.512
Cd _y Zn _{1-y} Te SOURCE A	○	.809	1.590
Cd _y Zn _{1-y} Te FILM A	△	.796	1.630
Cd _y Zn _{1-y} Te SOURCE B	◦	0.78	1.58
ZnTe (FILM)	▲	0	2.255
CdTe and ZnTe from Ref. 11	●		

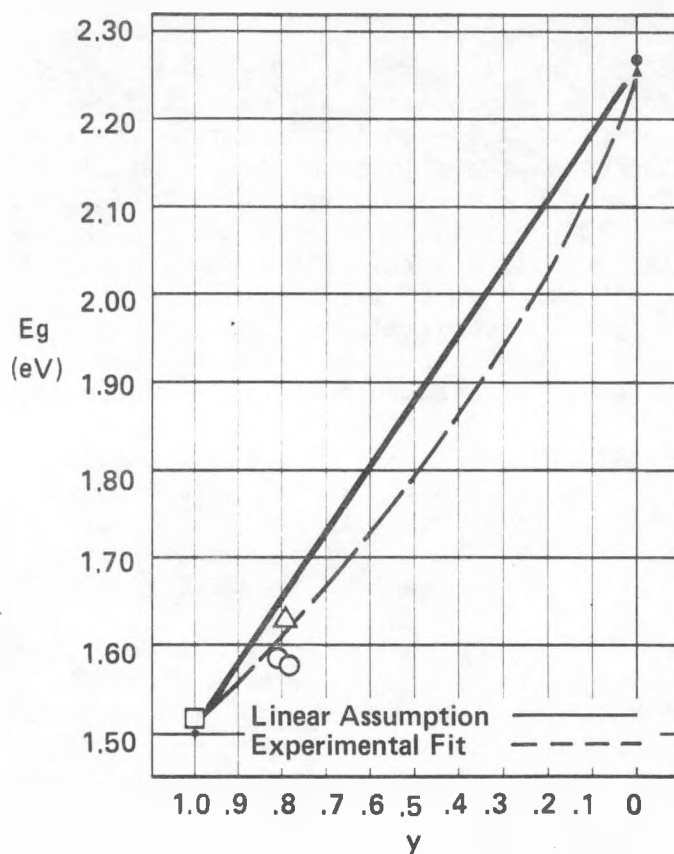


FIGURE 4. Optical Bandgap vs Composition for Cd_yZn_{1-y}Te

SACP measurements were only possible by reducing the resistivity of the films by annealing as discussed in the next section. Streaks and abrupt changes in darkness and contrast across the field of view are characteristic of charging problems and were found on all CdZnTe films. Charging problems are caused by high resistivity regions and became worse as the grain structure increased.

2.2 Annealing of Absorber Layers

The measured resistivities of as grown films of CdTe and CdZnTe are greater than $10^4 \Omega\text{-cm}$. The actual resistivities could be as high as $10^8 \Omega\text{-cm}$ but this value was outside the range of our measurement capability. After firing the films either at 600°C for 10 minutes or at 500°C for 30 minutes the resistivities are reduced to the $15\text{--}500 \Omega\text{-cm}$ range. The time required to anneal the films was determined from a $\sqrt{D_{\text{chem}} \cdot t}$ approximation where:

$$D_{\text{chem}} (\text{cm}^2/\text{sec}) = 4 \exp [-(1.15 \text{ eV}/kT)] \quad (1)$$

is the chemical diffusion coefficient^{1,2} in CdTe for the migration of native defects. All the Te-fired films of CdTe were p-type with room temperature Hall mobility ranging 25 to $75 \text{ cm}^2/\text{Vsec}$ and carrier concentrations varying from 5×10^{14} to $5 \times 10^{15} \text{ cm}^{-3}$. The mobility increased to as high as $180 \text{ cm}^2/\text{Vsec}$ at a reduced temperature of 195°K . The highest room temperature mobilities measured in bulk CdTe is about $70 \text{ cm}^2/\text{Vsec}$. The transport properties of these films could be limited by phonon scattering rather than either ionized impurity or ionized native defect scattering. A more detailed analyses of the mobility was not made because of scatter in the data for the same sample when recontacted. Contact to the p-CdTe was made with Au. Although better reproducibility may have been possible with Hg alloying (Section 3) the results were adequate to determine the effects of annealing.

It was not possible to obtain consistent Hall data for the CdZnTe films using Au contacts. I vs V examination of the contacts showed nonohmic behavior. However with Hg alloying Hall measurements showed the films to be p-type with room temperature concentrations of about 10^{16} cm^{-3} and corresponding mobilities about $30 \text{ cm}^2/\text{Vsec}$.

In the practical all thin film structure of Figure 1, CdZnTe would be deposited on polycrystalline n-type CdS. ZnTe would then in turn be deposited on the CdZnTe. Both the CdZnTe and the ZnTe layers would be high resistivity as grown. With subsequent controlled annealing at 500°C or less the ZnTe and then a fraction of the CdZnTe would become p-type. The optimum width of an intrinsic region could be controlled by proper annealing. Excessive anneal times could drive all or a fraction of the CdS film from n-type to semiinsulating resulting in a significant reduction in device performance.

3.0 P⁺ CONTACTS WITH Hg-ALLOYING

3.1 HgCdTe on Single Crystal CdTe Substrates

Single crystals of CdTe were used to evaluate the potential of contacting CdZnTe through Hg-alloying. HgCdTe was grown on single crystal CdTe substrates from 500°C to 600°C by a closed-space vapor epitaxial (CSVPE) technique^{13,14}. A HgTe source with an excess of Te and the substrate are positioned a few millimeters above the source and sealed off in an evacuated quartz ampoule. (Figure 5) Film composition x is determined by the temperature of growth. There are two components of growth; one due to vapor transport of the source constituents to the substrate surface, and a second due to the outdiffusion of Cd from the CdTe substrates to the CdHgTe. Films up to 50 micron in thickness with excellent lateral uniformity have been produced. The films produced normally have mirror-like surfaces in contrast with the irregularities seen on CdHgTe films produced by liquid phase epitaxy techniques. Films may be grown on any crystal plane of the CdTe substrate without significant effect upon the properties of the epitaxial film.

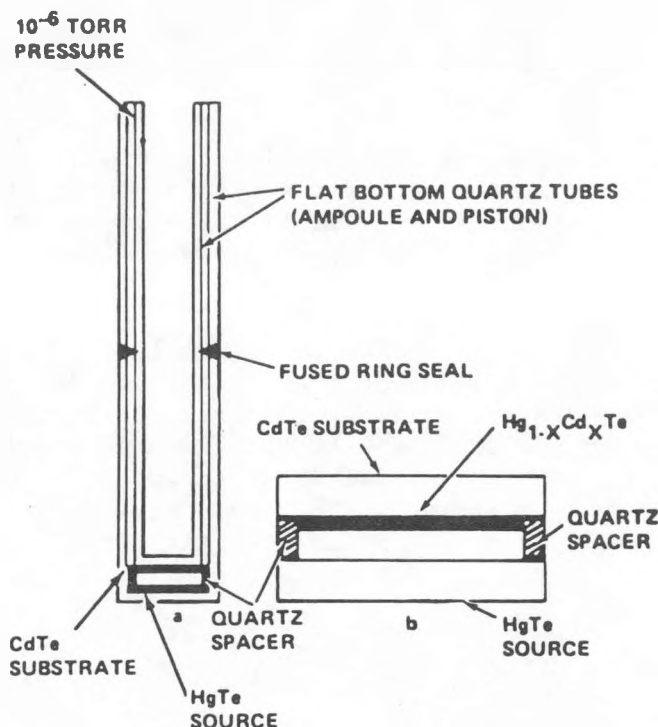


FIGURE 5. (a) Ampoule and (b) Enlargement of Source/Substrate Chamber for the Growth of CdHgTe by the Closed-Space Vapor Phase Expitaxy (CSVPE) Technique

The electrical properties of the HgCdTe films were measured by Hall measurements and their effectiveness as a contact were determined by through-the-film specific resistance (RA) measurements. Because of the high Hg content (i.e., $x \approx 0.25$) of these films, near intrinsic behavior and mixed conduction occur at room temperature. Therefore the extrinsic properties of the films are more easily determined at lower

temperature. At 77°K a hole concentration of $6 \times 10^{15} \text{ cm}^{-3}$ and hole mobility of $195 \text{ cm}^2/\text{Vsec}$ was determined for the CdHgTe films in Figure 6.

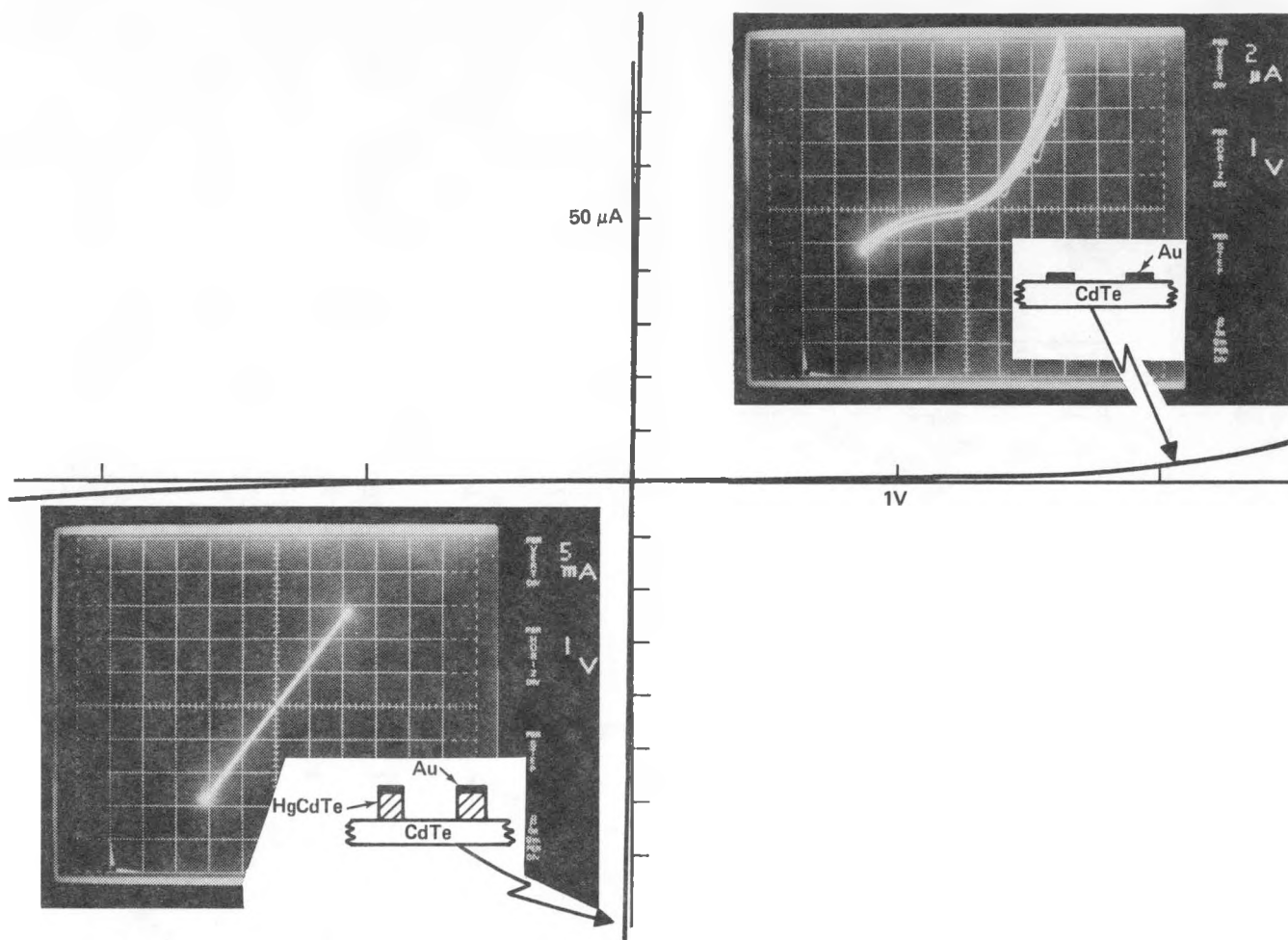


FIGURE 6. I vs V Characteristics for Au/CdTe and Au/CdHgTe/CdTe Structures

The effectiveness of an intermediate p-type HgCdTe layer as an ohmic contact between Au and CdTe was determined by comparing RA between Au/CdTe and Au/CdHgTe/CdTe structures shown in Figure 6. The structures were prepared by depositing 20 mil diameter Au dots on the HgCdTe layers which were about $10 \mu\text{m}$ thick. Using photolithographic techniques the exposed CdHgTe was etched beyond the CdHgTe/CdTe interface leaving the Au/CdHgTe/CdTe structure. In an adjacent region of the same wafer where the CdHgTe was removed Au dots were evaporated. The specific contact resistances of the two structures are compared in Figure 4-1. A zero bias the Au/CdTe structure has a resistance area product RA of $2 \times 10^6 \Omega\text{-cm}^2$. With the intermediate CdHgTe layer RA is less than $0.1 \Omega\text{-cm}^2$.

3.2 Hg-Alloys on CdZnTe Thin Films

Diffusion in the 500°C to 600°C temperature range results in excessive penetration of the Hg into the thin films. We are modifying the HgCdTe formation process to utilize processing temperatures below 500°C .

Two approaches were used to form the Hg-rich contacting layer. In the first approach Figure 7 1500 Å of SiO_2 was deposited at 100°C on an as-grown high resistivity CdZnTe thin film by photo-chemical vapor deposition. The SiO_2 was etched off at the corners of the sample. A few microns of HgCdZnTe were grown on the sample at 500°C. Examination of the region covered by the SiO_2 indicated some local penetration of Hg and subsequent HgCdZnTe growth at pores. However the SiO_2 provided a protective coating to the extent that electrical measurements showed the film to remain semi-insulating. Either deposition of the SiO_2 at a higher substrate temperature to provide denser SiO_2 or growth of the Hg alloy at lower temperatures could improve the SiO_2 as a protective coating.

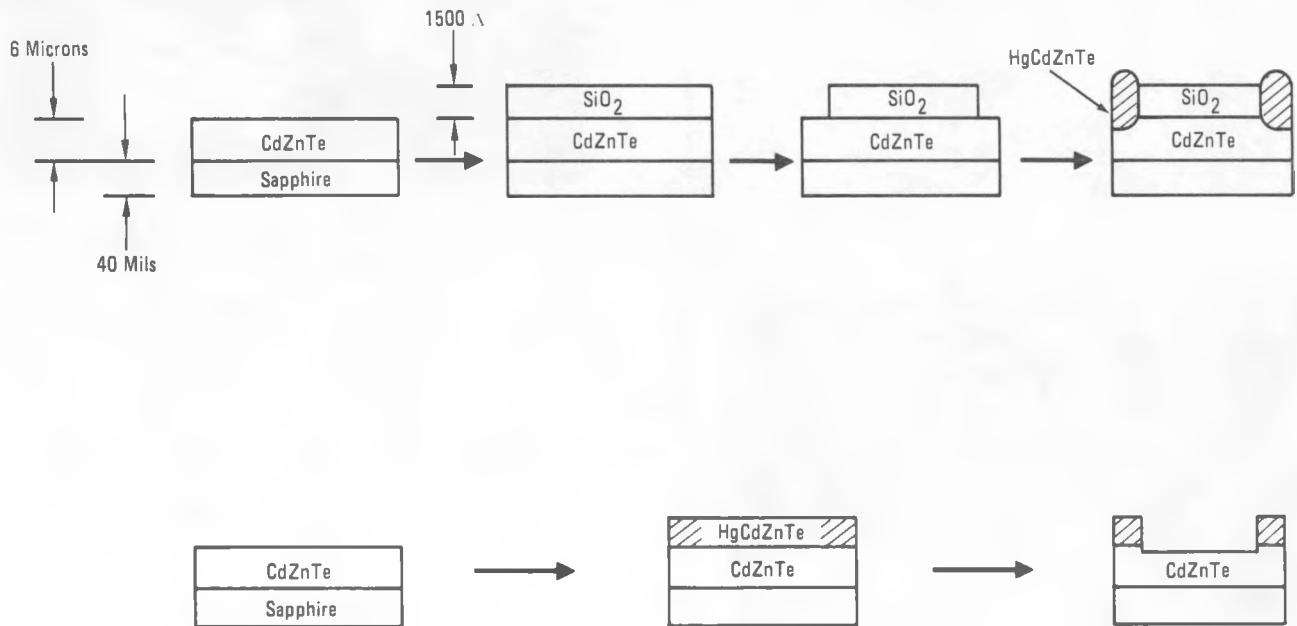


FIGURE 7. Formation of HgCdZnTe Contacts on CdZnTe Films by (Top) Selective Removal of SiO_2 Cap and Subsequent HgCdZnTe Growth and (Bottom) Growth and Selective Removal of HgCdZnTe Film

In a separate approach a few micron thick Hg alloy layer was grown on a CdZnTe film. Using photolithographic techniques the structure was etched so as to leave Hg-rich contacts at the corners of the sample. Hall measurements showed this sample to be p-type with a hole concentration of $7 \times 10^{15} \text{ cm}^{-3}$ and a mobility of $25 \text{ cm}^2/\text{V sec}$. With Hg alloys we were able to evaluate the electrical properties of p-type CdZnTe films.

3.3 Interdiffusion

An internal research effort was undertaken to investigate interdiffusion between Cd and Hg in CdHgTe alloys. In order to prepare suitable Hg rich contacts for this program it is necessary to predict the extent of the interdiffusion and shape of

the composition profile. We developed¹⁵ the following expression for the interdiffusion coefficient as a function of composition and temperature:

$$D_{\text{Cd}_x\text{Hg}_{1-x}\text{Te}} (\text{microns}^2/\text{sec}) = 3.15 \times 10^{10} \cdot 10^{(-3.53x)} \exp(-2.24 \times 10^4 / K) \quad (2)$$

Plots of this expression for $x=0$ and $x=1$ are in Figure 8. The diffusion coefficient is from 3 to 4 orders of magnitude larger in Hg-rich alloys than in Cd-rich alloys and from 400°C to 600°C varies about 2 orders of magnitude per hundred degrees. The corresponding activation energy and composition dependent parameters are respectively 1.93 eV and $10^{-3.53x}$. By specifying a specific width of the interdiffused contact region, W , and the processing time t , the processing temperature can be specified. Using a processing time of 15 minutes and contact region of 4000 Å in the approximation, $D_{\text{HgCdTe}} < W^2/t$, results in an interdiffusion coefficient of about 4×10^{-4} micron²/sec. This would correspond to a processing temperature of about 450°C.

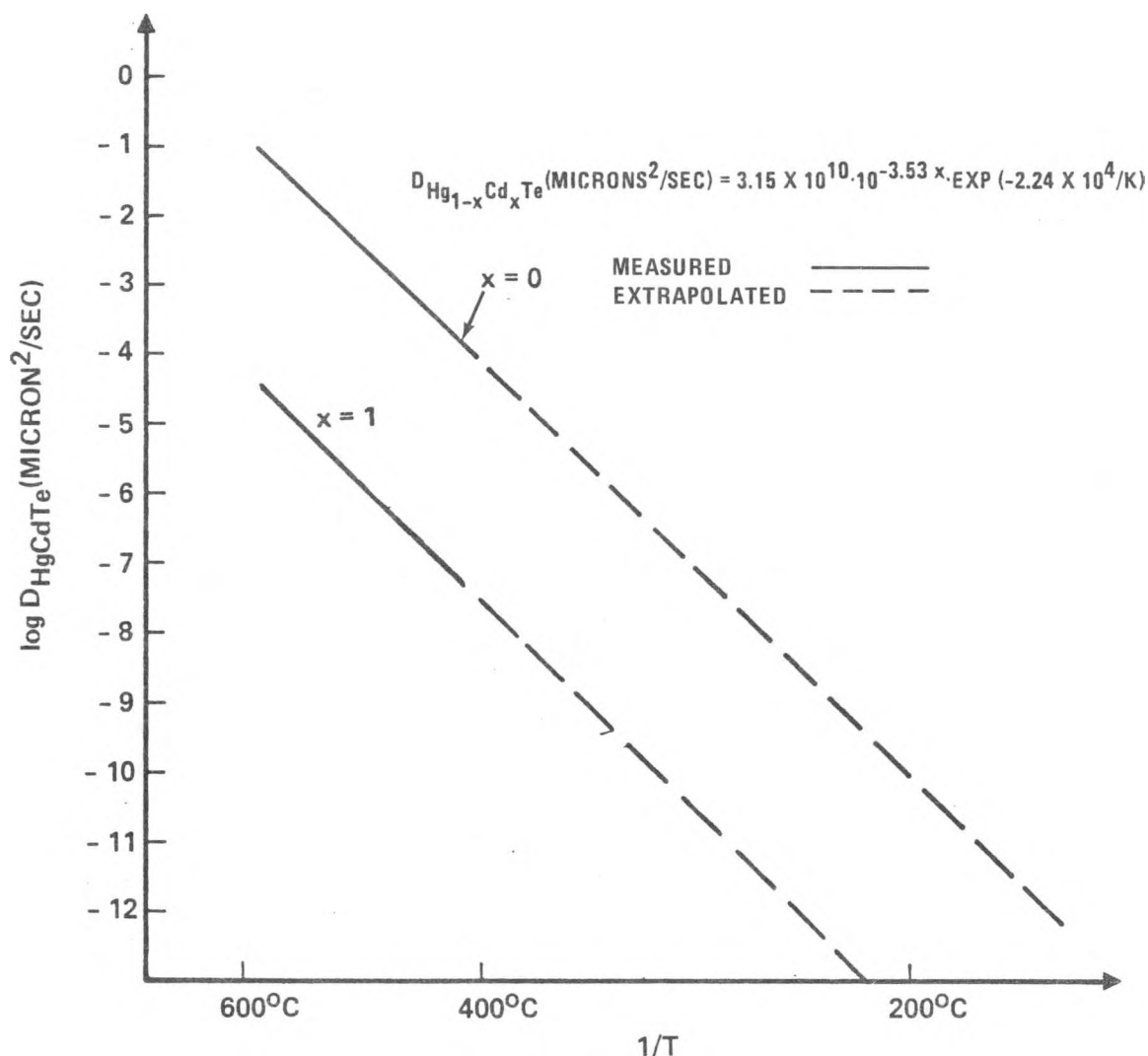


FIGURE 8. The Interdiffusion Coefficient for HgTe ($x = 0$) and CdTe ($x = 1$)

We also developed a growth/diffusion model and incorporated D_{CdHgTe} into the model to predict the composition profile. The model is applied here to the simple case of the growth of approximately a 10 micron thick layer of HgCdTe on a CdTe substrate at 525°C. Experimental data was taken on a beveled structure with the SERI microprobe. The model profiles are plotted on Figure 9 for a Cd fraction of 0.365 at the vapor solid interface, a growth temperature of 525°C and a deposition rate of 3.6 microns per hour. A Cd fraction of one(zero) corresponds to CdTe(HgTe). Profiles are shown for 85 minutes and 170 minutes of growth. The profiles for 170 minutes of growth and the microprobe data are in good agreement.

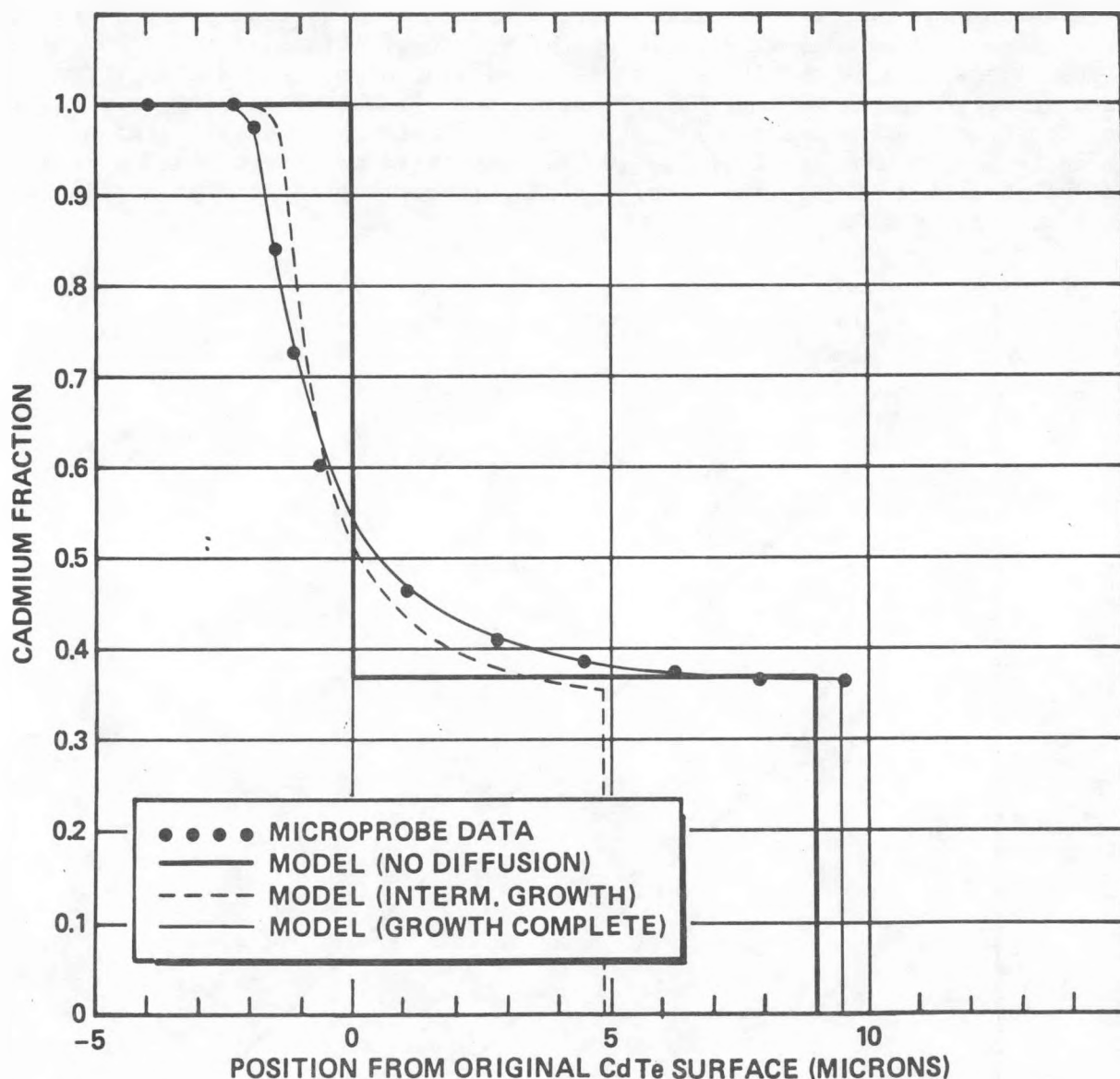


FIGURE 9. Cd Microprobe Data for $\text{Cd}_{0.36}\text{Hg}_{0.64}\text{Te}$ Deposited on CdTe by Closed Space Vapor Deposition at 525°C

The general behavior of interdiffusion in Hg alloys containing ZnTe are expected to be the same. However the rate of interdiffusion would be expected to be slower because the bond strength of ZnTe is greater than CdTe.

4.0 TRANSPARENT P-TYPE WINDOWS

It is expected that thin films of ZnTe can be made p-type and therefore could serve as a transparent window for the narrow bandgap cell. Preliminary studies to calibrate the rate of ZnTe deposition by congruent evaporation were made. Figure 10 shows a transmission spectrum of a 7.5 micron thick ZnTe film. A 7.5 micron thick rather than a thinner film was grown to more precisely calibrate the deposition rate. The optical value from the transmission data was 2.255 eV and is plotted in Figure 4.

An alternative method to preparing CdZnTe absorber layers and ZnTe-rich CdZnTe window layers is to grow a periodic structure of CdTe and ZnTe and interdiffuse the layer in an anneal subsequent to growth. As an initial test of the feasibility of this approach, we grew on 1 inch diameter sapphire a 25 layer periodic structure consisting of alternate 250 Angstrom thick ZnTe and 150 Angstrom thick CdTe films. The sapphire was not preheated in this preliminary run and therefore films were polycrystalline. There appears to be no obstacle in preparing these periodic structures with our UHV growth system. We will pursue this approach further only if difficulties arise with the growth of films from a single CdZnTe source.

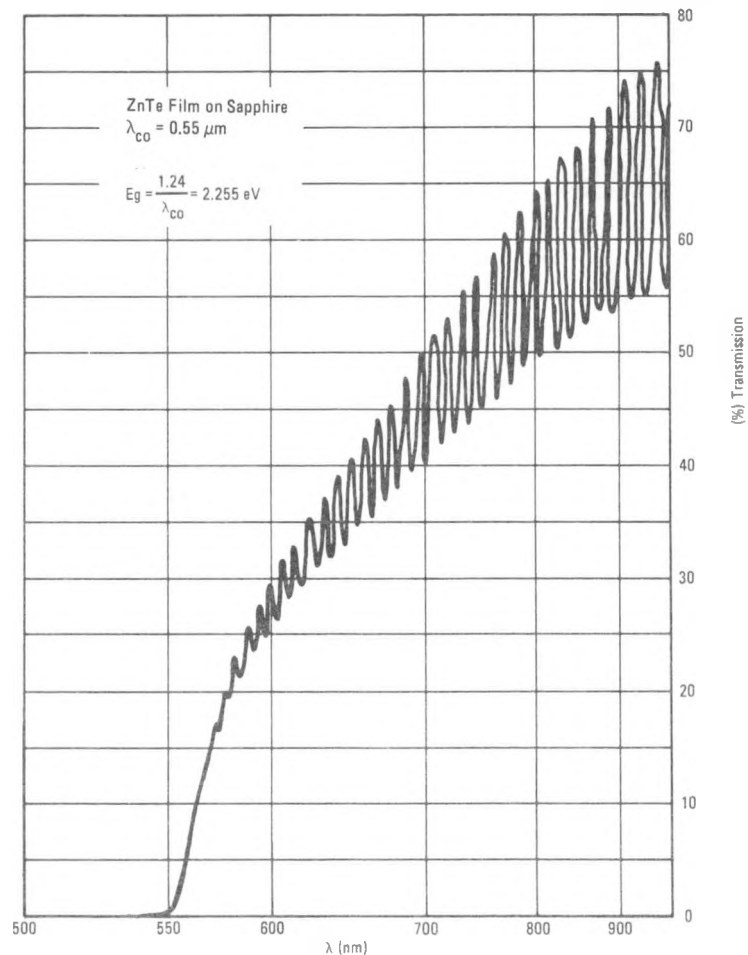


FIGURE 10. Transmission Spectrum for ZnTe Thin Film Prepared by Congruent Evaporation

5.0 CdZnTe DEVICES

Indium Schottky barriers were prepared on p-type single crystal and polycrystalline CdZnTe thin films. The best devices (Figure 11) showed barrier heights of about 0.9 eV and 0.5 eV for respectively single crystal and polycrystalline material. These results are encouraging. As discussed in the following section the next step is to evaluate the transport properties of the CdZnTe through a transparent CdS contact. As an additional step towards developing the practical all thin film cell, CdTe and CdZnTe films were deposited onto ITO/GLASS. Hg-rich alloys were subsequently grown on these composite structures.

The penetration of the Hg into these polycrystalline films will be examined. As discussed in the next section plans are to evaluate these polycrystalline structures as solar cells.

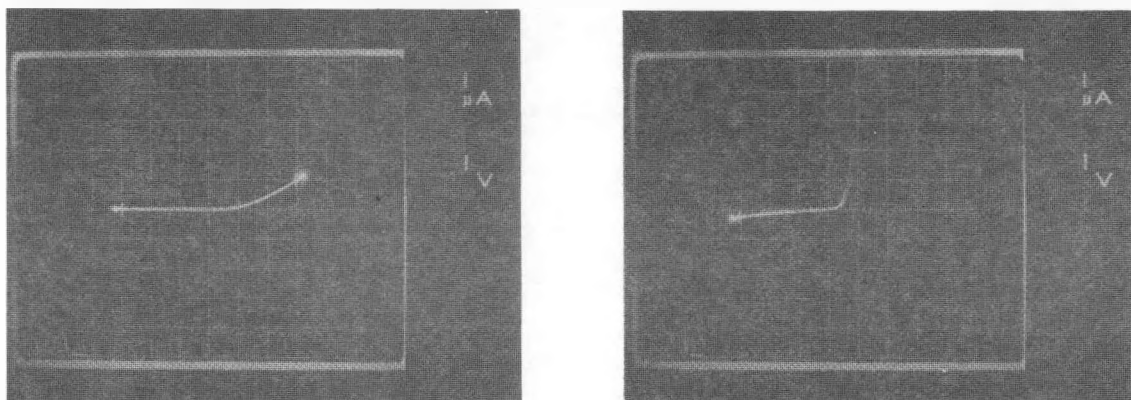


FIGURE 11. I vs V Characteristics for Indium Schottky Barriers on (Left) Single Crystal and (Right) Polycrystalline CdZnTe Thin Films Having 20 Percent Mole Fraction of ZnTe

6.0 PLANS

In the development of the all thin film CdZnTe/ITO/GLASS solar cell in Figure 1 test structures using sapphire substrates will continue to be used as a diagnostic tool. CdS will be evaporated on the CdZnTe/sapphire structure to determine the transport properties of the CdZnTe. Both single crystal and polycrystalline CdZnTe will be prepared. The effect of grain boundaries on the open current voltage and short circuit current of test cells will be measured.

In parallel studies to develop a p-type window, ZnTe films will be grown on sapphire. The processing conditions necessary to convert the films to p-type will be investigated. P⁺ HgZnTe contact will be made to the ZnTe by Hg vapor transport and subsequent diffusion. Effort to integrate the HgZnTe/ZnTe contact-absorber structures into the absorber will be initiated.

In developing the practical all thin film cell both ZnTe/CdZnTe/ITO/GLASS and ZnTe/CdZnTe/CdS/ITO/GLASS polycrystalline structures will be fabricated. The cell efficiencies will be measured. In particular the effect of the processing condition of the CdZnTe absorber layer on short circuit current and open current voltage will be examined.

REFERENCES

1. J. C. C. Fan, B.-Y. Tsaur and B. J. Pahn. 16th IEEE Photov. Spec. Conf., p. 692, (1982).
2. A. Hermann, K. Zweibel and R. Mitchell, 17th IEEE Photov. Spec. Conf., p. 911, (1984).
3. W. H. Bloss, J. Kimmerle, F. Pfisterer and H. W. Shock, 17th IEEE Photov. Spec. Conf., p. 715, (1984).
4. S. Wagner, J. L. Shay, K. J. Bachman and E. Buehler, Appl. Phys. Lett., 26, 229, (1975).
5. J. Steininger, J. Appl. Phys. 41, 2713 (1970).
6. F. F. Morehead and G. Mandel, Appl. Phys. Lett. 5, 53, (1964).
7. D. G. Thomas and E. A. Sadowski, Phys. Chem. Solids 25, 395 (1964).
8. T. F. Kuech and J. O. McCaldin, J. Appl. Phys. 53, 3121 (1982).
9. P. Migliorato and A. M. White, Solid State Electr., 26, 65 (1982).
10. K. Zanio, K. Hay, M. Massengill, and R. Bean. Presented at the IRIS Specialty Group on Infrared Detector, Seattle, WA, August 14-16, 1984.
11. Physics and Chemistry of II-VI Compounds, Edited by Aven and Prener, John Wiley & Son, NY, p. 335, 1967.
12. K. Zanio, Semiconductors and Semimetals 13, 125 (1978).
13. R. Kay, K. Zanio, F. Ju and J. Gilpin, presented at the U.S. Workshop on the Physics and Chemistry of HgCdTe, Dallas, TX, Feb. 8-10, 1983.
14. L. Svob, Y. Marfaing, Y. Triboulet, R. Bailey and G. Cohen, J. Appl. Phys. 46, 4251 (1975).
15. K. Zanio and T. Massopust, J. Electron Mater. 15 , 103 (1986).