

05
-3-82
(2)
5.37
SERI/TR-9196-1-T3
(DE82003590)

INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

Final Report for the Period June 1980-June 1981

MASTER

By
K. Zanio

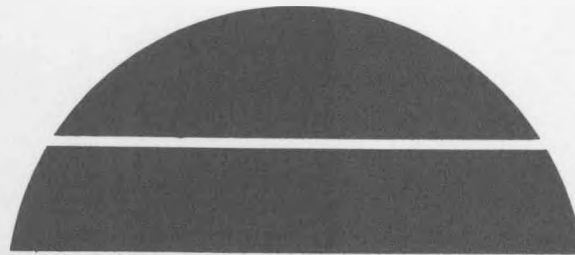
October 1981

SERI/TR--9196-1-T3

DE82 003590

Work Performed Under Contract No. AC02-77CH00178

Hughes Research Laboratories
Malibu, California



U.S. Department of Energy



Solar Energy

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.

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It
has been reproduced from the best available
copy to permit the broadest possible avail-
ability.

SERI/TR-9196-1-T3
(DE82003590)
Distribution Category UC-63

INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

K. Zanio

Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, CA 90265

October 1981

XZ-0-9196-1

Final Report
For period June 1980 through June 1981

Approved for public release; distribution unlimited.

Prepared for
DIVISION OF DISTRIBUTED SOLAR TECHNOLOGY
Washington, DC 20545

Monitored by
SOLAR ENERGY RESEARCH INSTITUTE
Photovoltaic Program Office
Golden, CO 30401

ABSTRACT

Thin-films of InP were grown on recrystallized CdS (RXCdS) and InP by planar reactive deposition for the purpose of determining the factors which limit the development of InP/RXCdS thin-film solar cells. InP films were grown on RXCdS at substrate temperatures of 380°C, 330°C, and 280°C; epitaxy of InP was achieved only at 280°C. An InCdS transition layer is present at temperatures above 300°C and may inhibit InP epitaxy. Be-doped films could not be made p-type on either RXCdS or semi-insulating (100) InP at a substrate temperature of 280°C. P-type behavior was only occasionally obtained at 330°C. At approximately 330°C, MBE data shows a transition from a reconstructed surface at a higher temperature to an atomically smooth surface at a lower temperature. A change in surface kinetics at this temperature may alter the doping mechanism. Therefore, the electron concentration was examined as a function of the ratio of the phosphorus to indium fluxes for unintentionally doped films prepared on (100) semi-insulating InP substrates at 330°C to alter the surface kinetics. No dependence of conductivity on deviations from stoichiometry was found. The growth of InP in a halide environment at reduced pressure is recommended as an alternative approach to enhance the growth of p-type InP at a lower substrate temperature. Growth of InP with PCl_3 was initiated at atmospheric pressure. Alternative device structures are presented which avoid the p-type doping problem.

PREFACE

This report was prepared by Dr. Kenneth Zanio of Hughes Research Laboratories, Malibu, California, a division of Hughes Aircraft Company, for the Photovoltaic Branch of the Division of Solar Energy of DOE under SERI contract XZ-0-9196-1. The technical monitors were Drs. Kim Mitchell and Richard Nottenburg at SERI in Golden, Colorado.

This program was undertaken by personnel in the Optical Physics Department under the supervision of Mr. M. Braunstein, Dr. R. Knechtli, and Dr. R.L. Abrams. The program manager was Dr. Zanio. Principal investigators were Dr. Zanio and Mr. F. Krajenbrink. Important contributions to the program were made by Messrs. K. Miller, P. Hoberg, H. Montano, and A. Timper. SIMS analyses were undertaken by Hanford Engineering Development Laboratory (HEDL) under separate contract to SERI. Valuable discussion with Dr. David Greenslade of HEDL is acknowledged. Additional SIMS and Auger services were purchased from Charles Evans and Associates through this contract.

TABLE OF CONTENTS

SECTION	PAGE
1 INTRODUCTION	1
2 BACKGROUND	3
A. The RxCdS/Glass Substrate	3
B. Planar Reactive Deposition	5
1. Description of the System	5
2. InP Epitaxy	5
3 TECHNICAL EFFORT	11
A. P-Type Doping	11
B. Zn Doping	18
C. N-Type Doping By Native Defects or Impurities	18
D. Analyses for Impurities	24
E. InP Epitaxy on RxCdS	32
F. InP Growth with Halides	44
4 SUMMARY AND RECOMMENDATIONS	49
5 REFERENCES	53
APPENDIX	55

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Optical and x-ray Read pictures of a thermally deposited and unrecrystallized CdS film, an incompletely recrystallized CdS film, and a fully recrystallized CdS film	4
2	Cross section of PRD source/substrate assembly	6
3	Planar reactive deposition system used for the preparation of InP	7
4	I versus V of CdS/InP cell with intermediate InP layer prepared by PRD at 360°C	8
5	InP deposited by PRD at 280°C on a single RXCdS grain, two RXCdS grains, and the same two RXCdS grains, but with the grain boundary delineated	10
6	Type and carrier concentration of Be-doped InP films prepared at various substrate temperatures versus the number of depositions with the same source	12
7	Microprobe analysis of Be-doped InP film showing about 1 percent Al	13
8	SEM and corresponding SAD pictures of Be/Al doped InP films prepared at 330°C containing less than 1 percent and approximately 1 percent of Al	14
9	SIMS profiles of p-InP/InP for InP prepared at 380°C	16
10	SIMS profiles of n-InP/InP for InP prepared at 300°C	17
11	Zn doped InP prepared by PRD	19
12	Unintentionally doped InP films prepared on InP substrates by vacuum technologies	20
13	InP surface structure above 320°C with surface reconstruction, and below 320°C without surface reconstruction	22
14	Electron concentration of undoped InP prepared at 330°C versus the ratio of the reactants	23
15a	SIMS analysis of surface of In source and pure In foil for mass 1 through 50	25

FIGURE		PAGE
15b	SIMS analysis of surface of In source and pure In foil for mass 51 through 100	26
15c	SIMS analysis of surface on In source and pure In foil for mass 101 through 150	27
15d	SIMS analysis of surface of In source and pure In foil for mass 151 through 200	28
15e	SIMS analysis of surface of In source and pure In foil for mass 201 through 250	29
16	SIMS depth profile of ^9Be , ^{27}Al , ^{40}Ca , ^{56}Fe and ^{69}Ga in In source	30
17	Residual gas spectra outside LN_2 shrouds	32
18	Scanning electron microscope picture of InP/RXCdS/ITO/GLASS structure	34
19	SEM and x-ray Read pictures of InP deposited on RXCdS at different substrate temperatures	35
20	Scanning electron microscope picture of InP deposited on the ITO/GLASS substrate, the outside of the RXCdS mesa and the interior of the RXCdS mesa	37
21	Scanning electron microscope picture of two grains of InP at 45° with respect to the plane of the film and 65° with respect to the plane of the film	38
22	SIMS profiles of p-InP/RXCdS for InP deposited at 380°C	40
23	SIMS profiles of n-InP/RXCdS for InP prepared at 330°C	42
24	Low pressure InP/ PCl_3 system	45
25	Low pressure InP/ PCl_3 reactor	46
26	All-thin-film InP/CdS solar cells utilizing the backwall and frontwall structures	47

SECTION 1

INTRODUCTION

CdS/InP* thin-film solar cells consisting of CdS deposited on micron size InP grains have been prepared with efficiencies of 5.7 percent at air mass two¹(AM2). These efficiencies are primarily limited by grain boundaries. If the effect of grain boundaries could be reduced, single crystal efficiencies of 15 percent could be approached. The objective of our studies was to further develop the InP/CdS system by preparing InP on a suitable large grained substrate. In an earlier program (Contract XJ-9-8170-1) supported by DoE, we had successfully developed a substrate having large grains of recrystallized CdS (RXCdS) with lateral dimensions of about 50 μm (see Appendix A). In order to prevent the decomposition of RXCdS during the subsequent deposition of InP we developed planar reactive deposition (PRD), a low temperature process, for depositing InP. With this process we prepared 10 percent efficient CdS/InP single crystal cells. However, we have been unable to prepare thin-film cells consisting of InP on RXCdS. The primary problems are the difficulty in preparing p-type InP at temperatures below 320°C and the difficulty of obtaining good InP epitaxy on RXCdS above this temperature.

In Section 2 we will summarize our techniques for preparing large grains of RXCdS and depositing InP by PRD. In Section 3 we will summarize our additional technical effort this period to prepare epitaxial p-type InP on RXCdS. In the last section we will recommend what further steps should be taken to develop the InP/CdS system.

*CdS/InP refers here to a structure in which CdS has been deposited on InP. Similarly, InP/CdS refers to a structure in which InP has been deposited on CdS.

SECTION 2

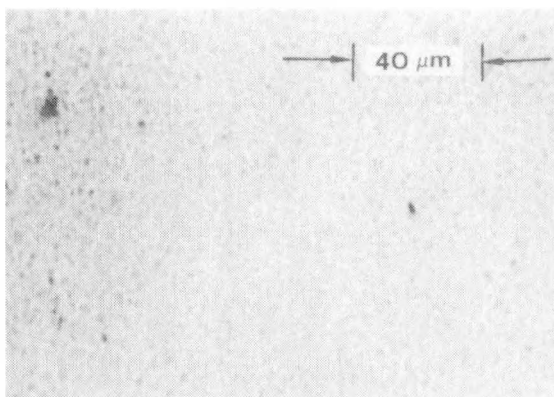
BACKGROUND

A. THE RXCdS/GLASS SUBSTRATE

The development of InP, as well as GaAs thin-film systems, has been restricted by the unavailability of a low cost substrate. Fortunately, in the InP system a low cost substrate consisting of large grains of RXCdS is available. The first step in preparing the RXCdS is to vacuum deposit about 20 μm of CdS on ITO/GLASS at a substrate temperature of about 200°C. The CdS is recrystallized in flowing H_2S at 500°C for about 30 min. Figure 1 shows optical (left) and x-ray Read (right) pictures of CdS films at different stages of processing. The thermally deposited films consist of submicrometer size grains. The preferred orientation of the grains are such that the c axis is aligned normal to the substrate. The preferred orientation results in arcs rather than continuous rings on the x-ray Read picture. As the recrystallization process proceeds the grain size increases and the grains adopt a more random orientation. The Read picture of the incompletely recrystallized film (middle) contains both arcs characteristic of submicrometer grains of preferred orientation, and random discrete spots characteristic of large grains of randomly oriented CdS. Clusters of discrete spots also indicate that a small fraction of the large grains have a preferred orientation. Only discrete spots are found in the picture (bottom) for the fully recrystallized film. The average grain size of our films is about 40 μm . Grains with lateral dimensions up to 0.2 mm have been observed. After films are recrystallized, the sheet resistance is in excess of $10^5 \Omega/\square$. However, by firing RXCdS in a Cd overpressure at 500°C, the sheet resistivity is reduced to a typical value of about 20 $\Omega/\square$. Values as low as 10 $\Omega/\square$ have been obtained. Absorption losses are about 10 percent over wavelengths ranging from 0.5 to 1.0 μm .

Further details regarding the preparation and characterization of the RXCdS substrate are contained in the 1979 final report to DoE contract XJ-9-8170-1.

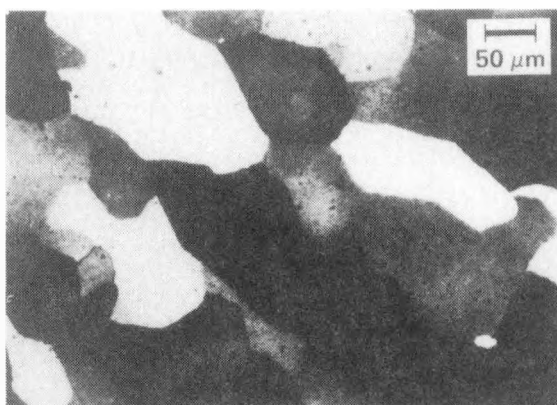
OPTICAL



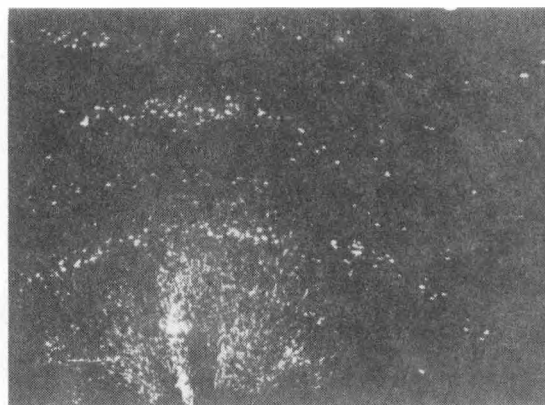
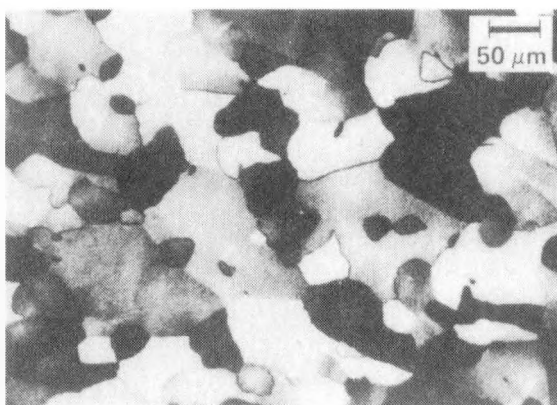
X-RAY READ



THERMALLY DEPOSITED CdS



INCOMPLETELY RECRYSTALLIZED CdS



FULLY RECRYSTALLIZED CdS

Figure 1. Optical (left) and x-ray Read (right) pictures of (top) a thermally deposited and unrecrystallized CdS film, (middle) an incompletely recrystallized CdS film, and (bottom) a fully recrystallized CdS film. Photographs of the thermally deposited films were taken in unpolarized light, whereas photographs of the recrystallized films were taken in transmitted polarized light.

B. PLANAR REACTIVE DEPOSITION

1. Description of the System

Development of a terrestrial thin-film solar cell requires an economical process for preparing the cell. Because CdS decomposes easily a low temperature process is also required. Conventional chemical vapor deposition systems operate at an excessive temperature. Molecular beam epitaxy can operate at lower temperatures, but in its present form is uneconomical. With internal and AFOSR funding on F44620-76-C-0133 we developed the planar reactive deposition technique. In the preparation of InP, In metal is evaporated from a broad graphite crucible (Figure 2). A PH_3/H_2 gas mixture enters the crucible from the bottom of the crucible. The PH_3 gas decomposes in the In source cavity and In, P_4 , and H_2 stream onto the substrates. The substrates are located on a stainless steel plate which rides on bearings so the substrates can be positioned above another PRD chamber for the preparation of multilayer films. Two such PRD units are contained within a metal vacuum chamber (Figure 3). A turbomolecular pump exhausts the vacuum chamber to a base pressure of about 10^{-8} Torr when the shrouds surrounding the PRD units are filled with LN_2 .

2. InP Epitaxy

a. Epitaxy on Single Crystal InP

InP was deposited on (100) semi-insulating substrates over the temperature range of 225 to 410°C to evaluate the process. Single crystal epitaxy was achieved at temperatures as low as 260°C . Unintentionally doped films are n-type with room temperature mobilities as high as $4,010 \text{ cm}^2/\text{Vsec}$ at the higher substrate temperatures. Beryllium was added to the source to make p-type material.

Single crystal solar cells, as shown in Figure 4, were prepared. A p-type layer a few microns thick was deposited on $\text{p}^+\text{-InP}$ at a substrate temperature of about 360°C . N-type CdS and an In grid were deposited to complete the cell. No anti-reflective coatings were used. AM2 efficiencies up to 10 percent were obtained for illuminated areas of 24 mm^2 . Polycrystalline CdS/InP cells were also prepared by depositing polycrystalline InP on $\text{p}^+\text{-InP}$ substrates. Efficiencies of only a few percent were obtained. Since the loss of efficiency was

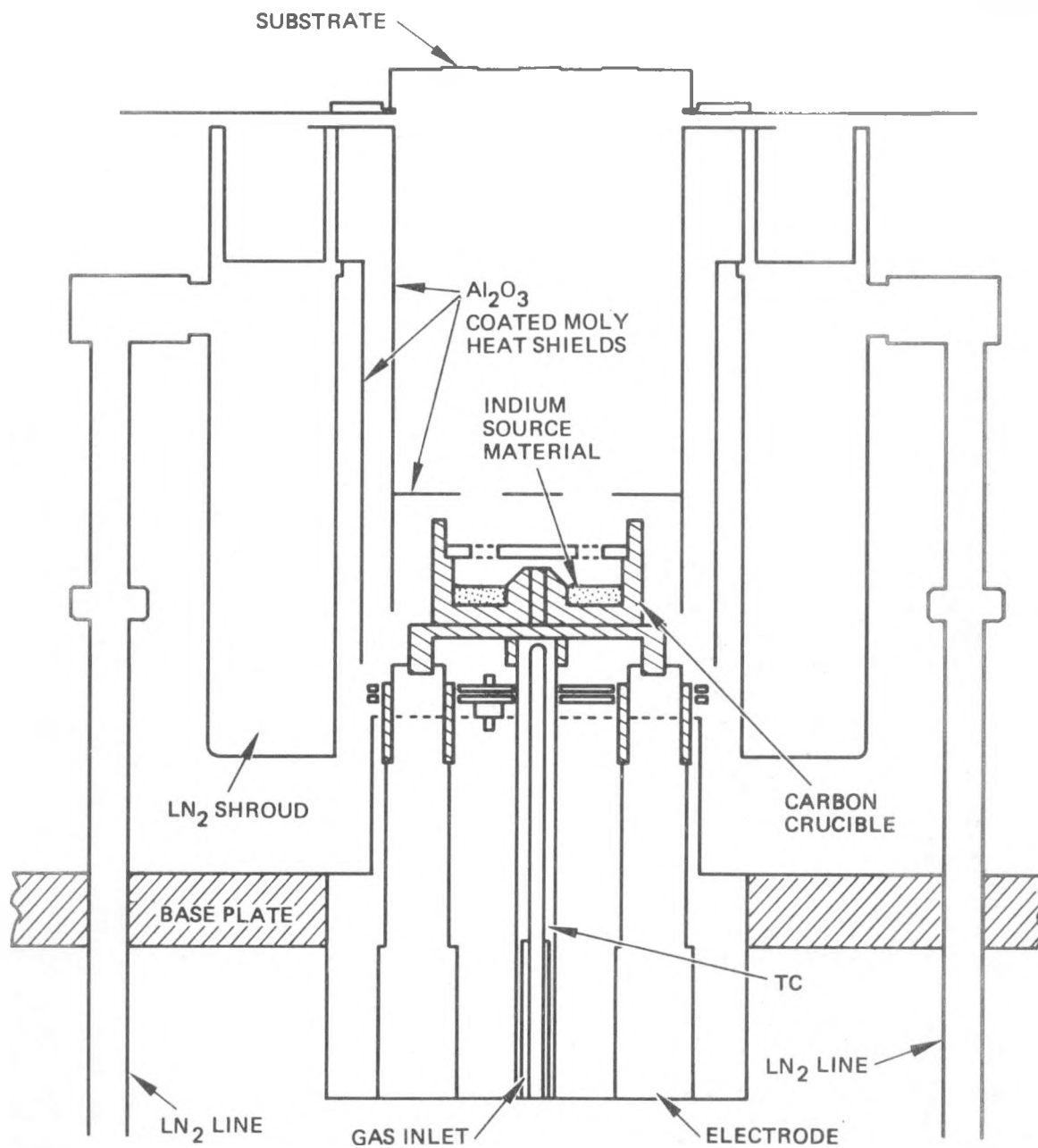


Figure 2. Cross section of PRD source/substrate assembly.

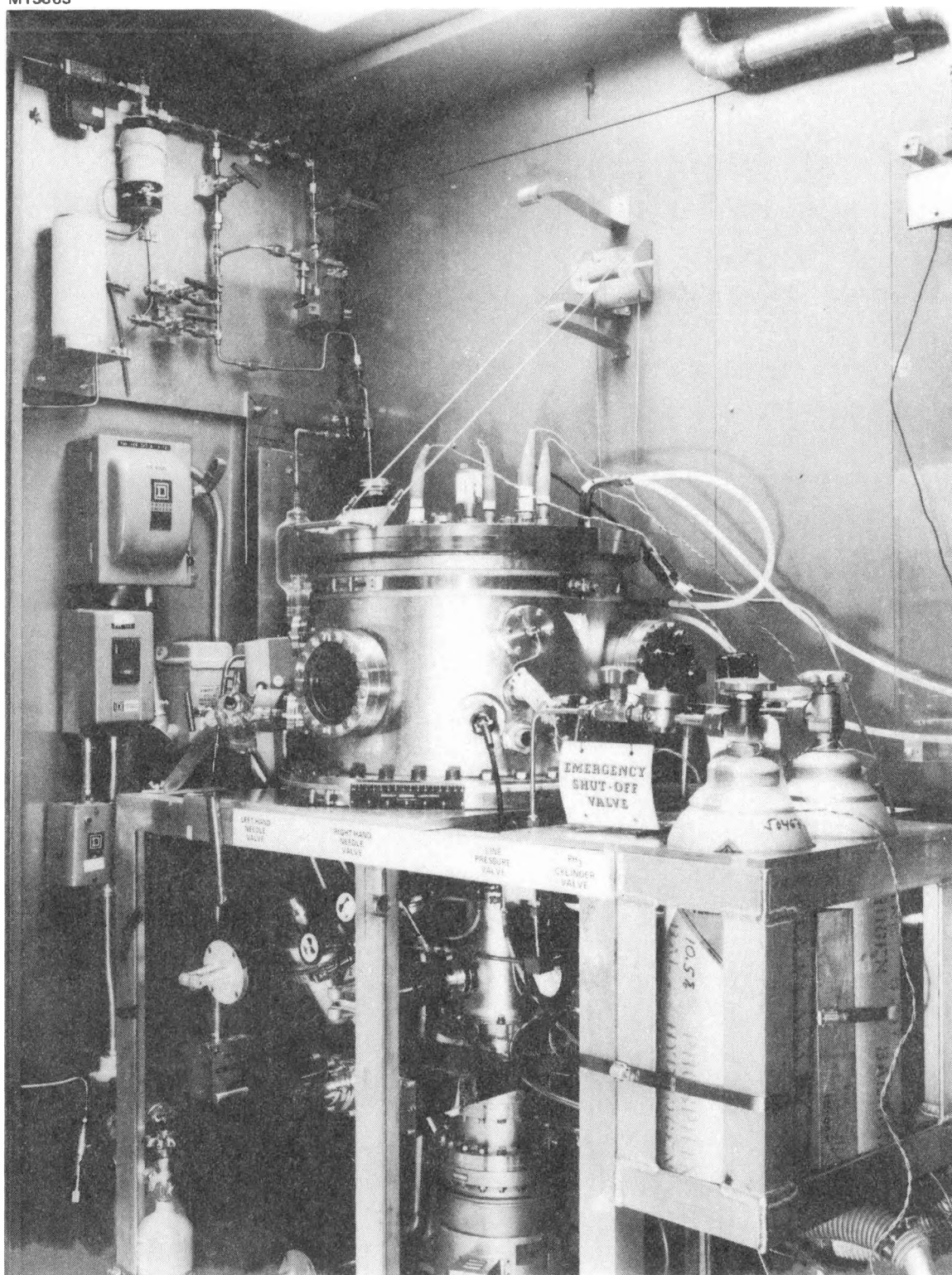


Figure 3. Planar reactive deposition system (foreground) used for the preparation of InP.

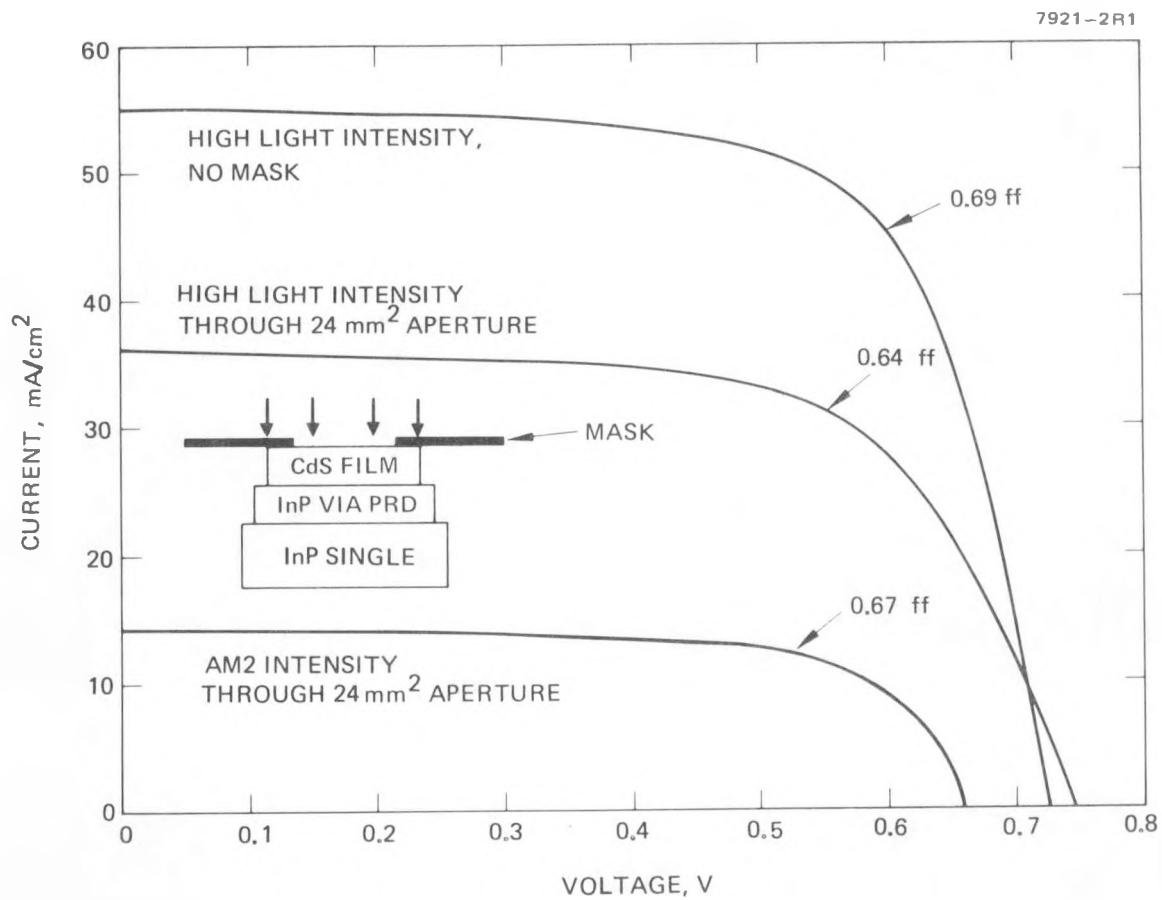


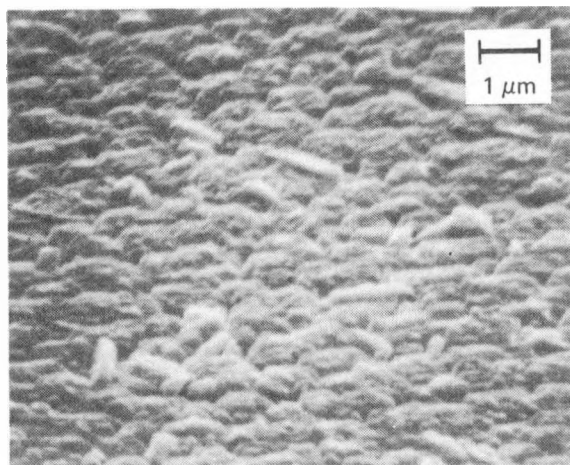
Figure 4. I versus V of CdS/InP cell with intermediate InP layer prepared by PRD at 360°C .

primarily due to a reduced open circuit voltage, we associated the reduced efficiency to the presence of grain boundaries.

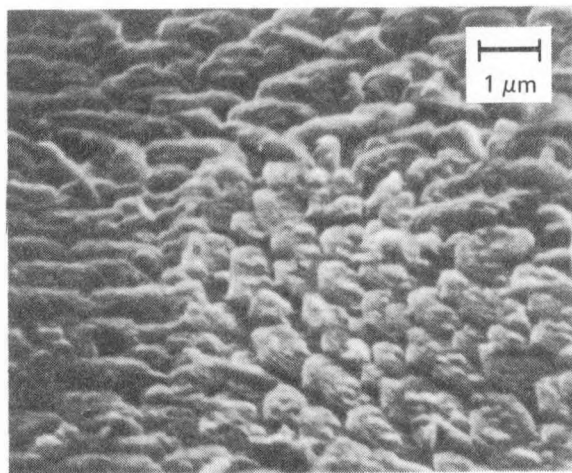
b. Epitaxy on RXCdS

After establishing that the quality of our layers was adequate for solar cells we undertook the deposition of InP on RXCdS at 280°C and 380°C. The lateral dimensions of the InP grains prepared at 380°C were only about 1 μm and are much smaller than the lateral dimensions of the RXCdS. Devices were prepared on 5- μm -thick p-type films at 380°C, and exhibited blocking action; no light response was observed. It is possible that an intermediate n-InP light blocking layer exists and that holes are generated tens of diffusions lengths from the p-n junction.

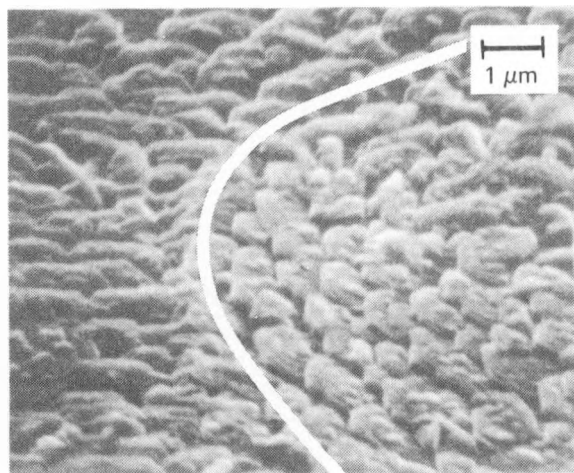
Epitaxy was obtained at 280°C on the RXCdS grains, which have dimensions of about 40 μm . Figure 5 (top) shows SEM pictures of InP epitaxy on a single RXCdS grain. Only at higher magnifications can the facets of the grains be resolved. It is evident that the facets are aligned over the entire photograph. The middle picture shows InP epitaxy covering two adjacent grains of RXCdS. There is a distinct difference in the orientation of the facets across the grain boundary. In the bottom picture, this grain boundary is delineated to better contrast the orientation of the two grains. We could not establish the conditions to routinely obtain epitaxy of InP on RXCdS.



InP ON SINGLE
RXCdS GRAIN



InP ON TWO
RXCdS GRAINS



InP ON TWO
RXCdS GRAINS
(GRAIN BOUNDARY
DELINEATED)

Figure 5. InP deposited by PRD at 280°C on (top) a single RXCdS grain, (middle) two RXCdS grains, and (bottom) the same two RXCdS grains, but with the grain boundary delineated.

SECTION 3

TECHNICAL EFFORT

A. P-TYPE DOPING

We had previously found that Be-doped InP films prepared on RXCdS at 280°C were n-type, even though the RXCdS was capped with InP to prevent n-type doping via sulfur vapor transport. We therefore deposited Be-doped InP on semi-insulating InP substrates to investigate this problem in more detail. Figure 6 shows the general behavior of the type and carrier concentration for several runs subsequent to charging In sources to similar levels of Be. Each point refers to data taken on either one sample or an average over either two or three samples. The degree of p-type electrical activity is strongly dependent on the substrate temperature. At a substrate temperature of 380°C, the films are strongly p-type for the first few runs. After the fourth or fifth deposition, the films are n-type. The films become either weakly compensated (solid line) or, less frequently, highly compensated (dashed line). At a substrate temperature of 300°C or below, p-type films are never obtained. The electron concentration varies by two orders of magnitude (see Section 3.C for data on unintentionally undoped films.) Both n- and p-type results are obtained at 330°C.

It was not established that Be was present in our films. Therefore, we examined our films for Be with a microprobe and with SIMS. Our microprobe was not sensitive enough to detect Be. However, Al was detected in some of our films at about 1 percent (see Figure 7). When our films, indicated by the dots, are compared with the InP reference substrate, an Al peak (delineated by an arrow) becomes apparent to the left of the phosphorus peak. At high levels of Al, and presumably also of Be, the quality of the epitaxy is often degraded. Figure 8 shows SEM and corresponding selective area electron diffraction (SAD) pictures of a layer containing ~1 percent Al. This figure also contains SEM and SAD pictures of a layer having less than 1 percent Al. The SEM shows the surfaces to be rougher for the more heavily doped layer. There is no difference in the channeling pattern between the substrate and the film for the film containing less than 1 percent Al.

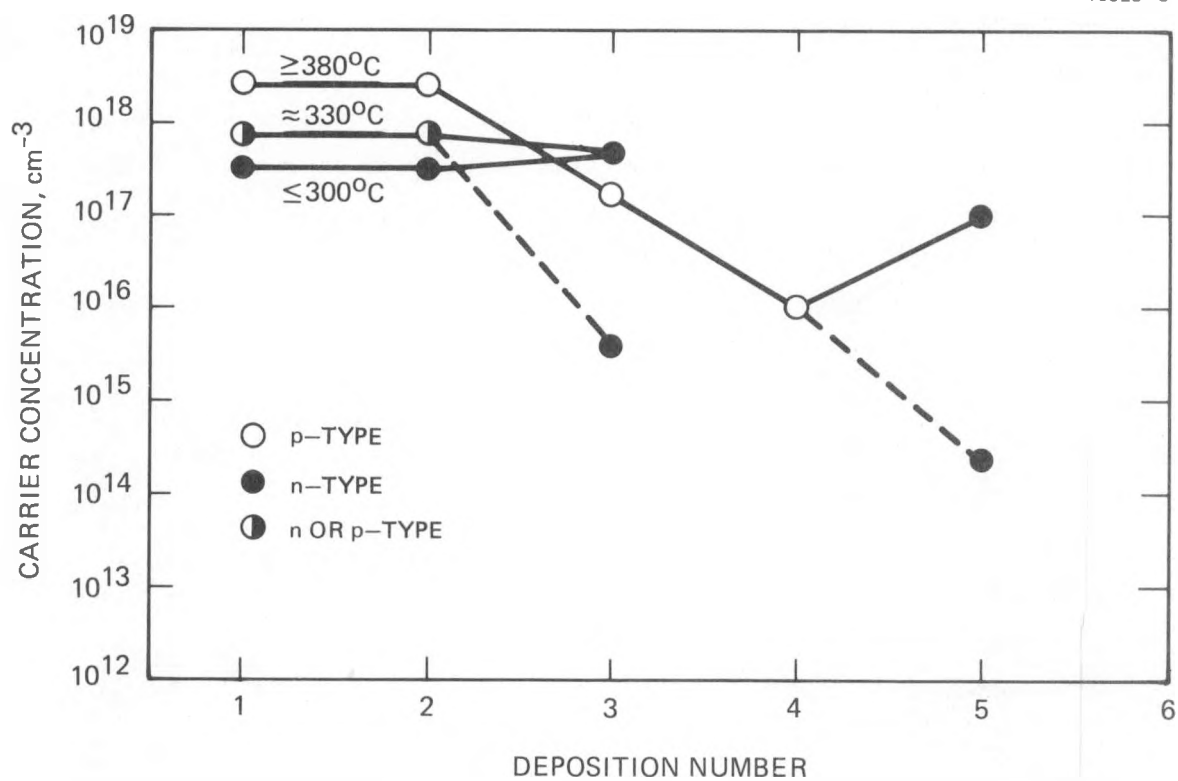


Figure 6. Type and carrier concentration of Be-doped InP films prepared at various substrate temperatures versus the number of depositions with the same source.

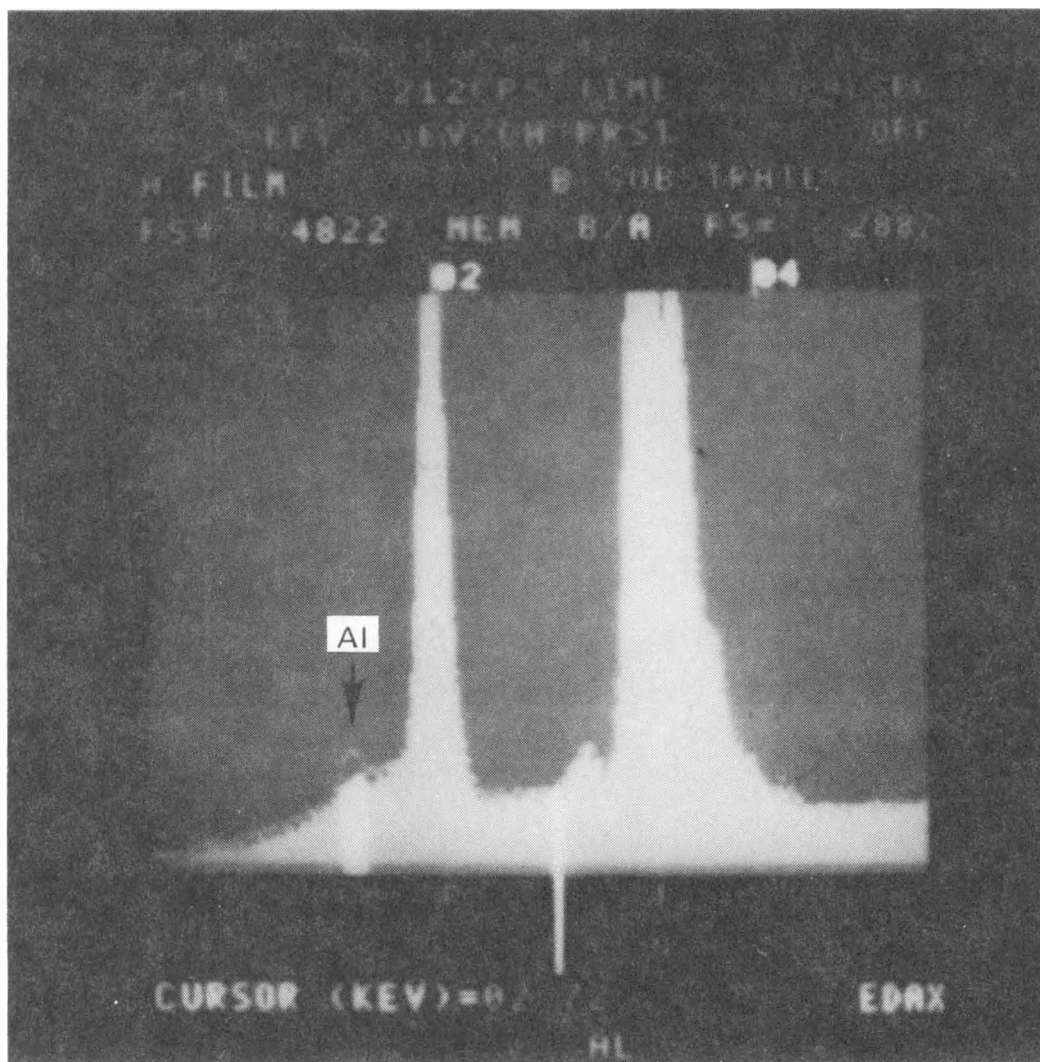
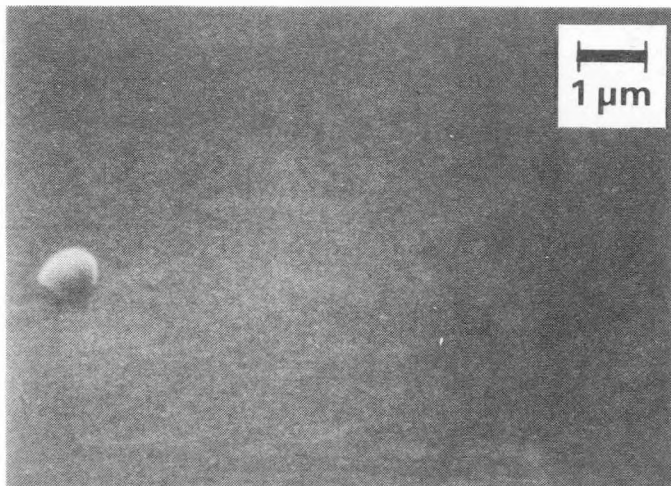
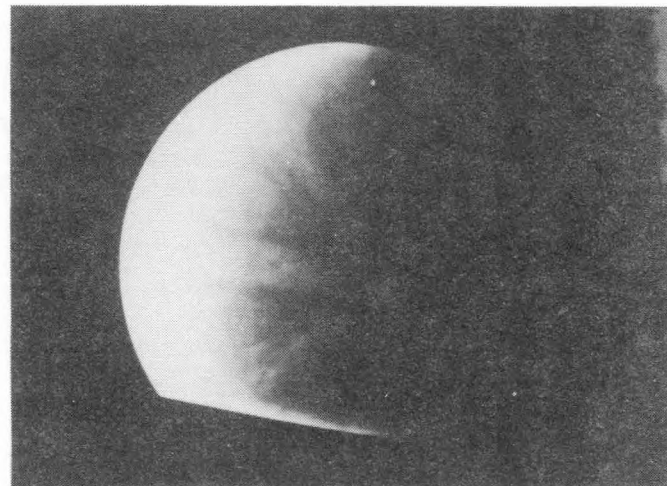


Figure 7. Microprobe analysis of Be-doped InP film showing about 1 percent Al.

SEM



SAD



10528-3

14

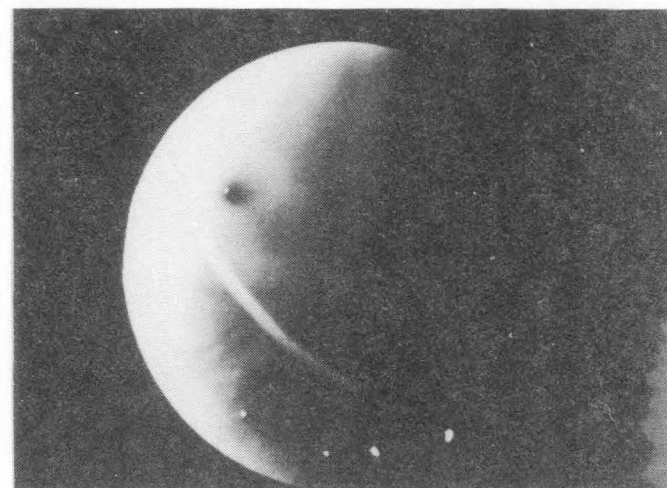
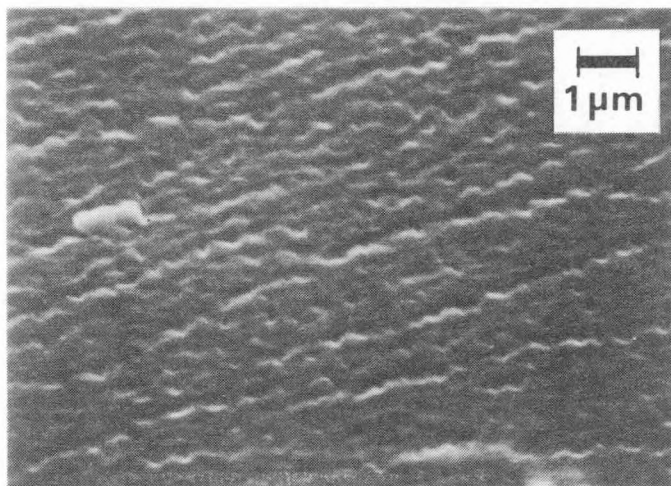


Figure 8. SEM and corresponding SAD pictures of Be/Al doped InP films prepared at 330°C containing (top) less than 1 percent and (bottom) approximately 1 percent of Al.

However, for the film containing 1 percent Al, the channeling pattern of the substrate is superior to that of the film. For more precise determination of the impurities, SIMS analysis was undertaken by Hanford Engineering Development Laboratory under contract to SERI. An oxygen beam was used to excite secondary ions. The secondary ion intensity was recorded in counts per second rather than atoms per cm^3 , since no standards were available to make the conversion. (To find counts per second for each specie, multiply the abscissa by the factors in the legend.) Those samples analyzed were taken from a run in which a freshly charged source was used corresponding to position 1 on the ordinate in Figure 6. Figure 9 shows SIMS profiles for In, P, Be, Al, and Ga for a 4.6 μm -thick p-type InP film prepared on semi-insulating InP at a substrate temperature of 380°C. The degree of abruptness in the Be, Al, and Ga profiles at the interface is limited by machine sensitivity. The actual profiles are more abrupt. Gallium is present because it is used in our system to wet the source heater plate to the water-cooled Cu electrodes. Al is present in the SIMS data because the Be is incorporated in the In source as a 5 percent/95 percent by weight Be/Al alloy. Ga and Al are isoelectronic impurities, and if incorporated uniformly in the InP at less than 1 percent, are not expected to significantly affect the electrical, optical, and crystallographic properties of our films.

Figure 10 is a SIMS profile for P, Be, Al, and Ga in Be-doped 0.7- μm -thick InP film prepared at an InP substrate temperature of 300°C. As expected, Be was present. Although we determined Be and other impurities to be present in our n-type films we could not determine their concentrations because standards were not available. The slopes at the thin-film/substrate interface for Be, Al, and Ga are limited by the resolution of the SIMS. The slopes for Al and Ga are more abrupt than for Be because of better statistics for Al and Ga. The profiles at 300°C are more abrupt in Figure 10 than in Figure 9 and are probably due to differences in the sputtering rates. The sputtering rate for the 4.6- μm -thick film prepared at 380°C is faster than the rate for the 0.7- μm -thick film prepared at 300°C. Consequently, the spatial resolution for the film prepared at 300°C is more detailed than for the film prepared at 380°C. We rule out that the profile at the interface is characteristic of

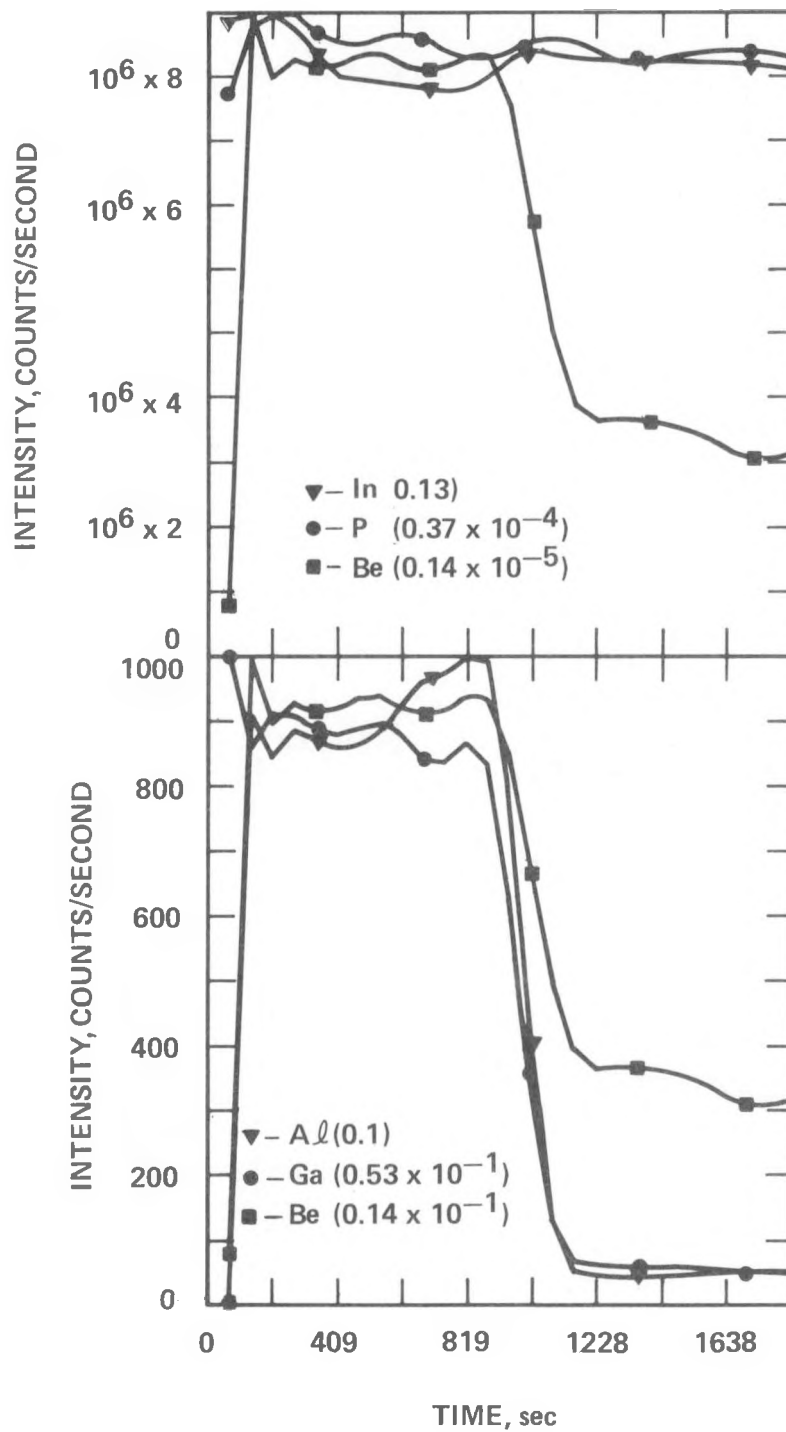


Figure 9. SIMS profiles of p-InP/InP for InP prepared at 380°C.

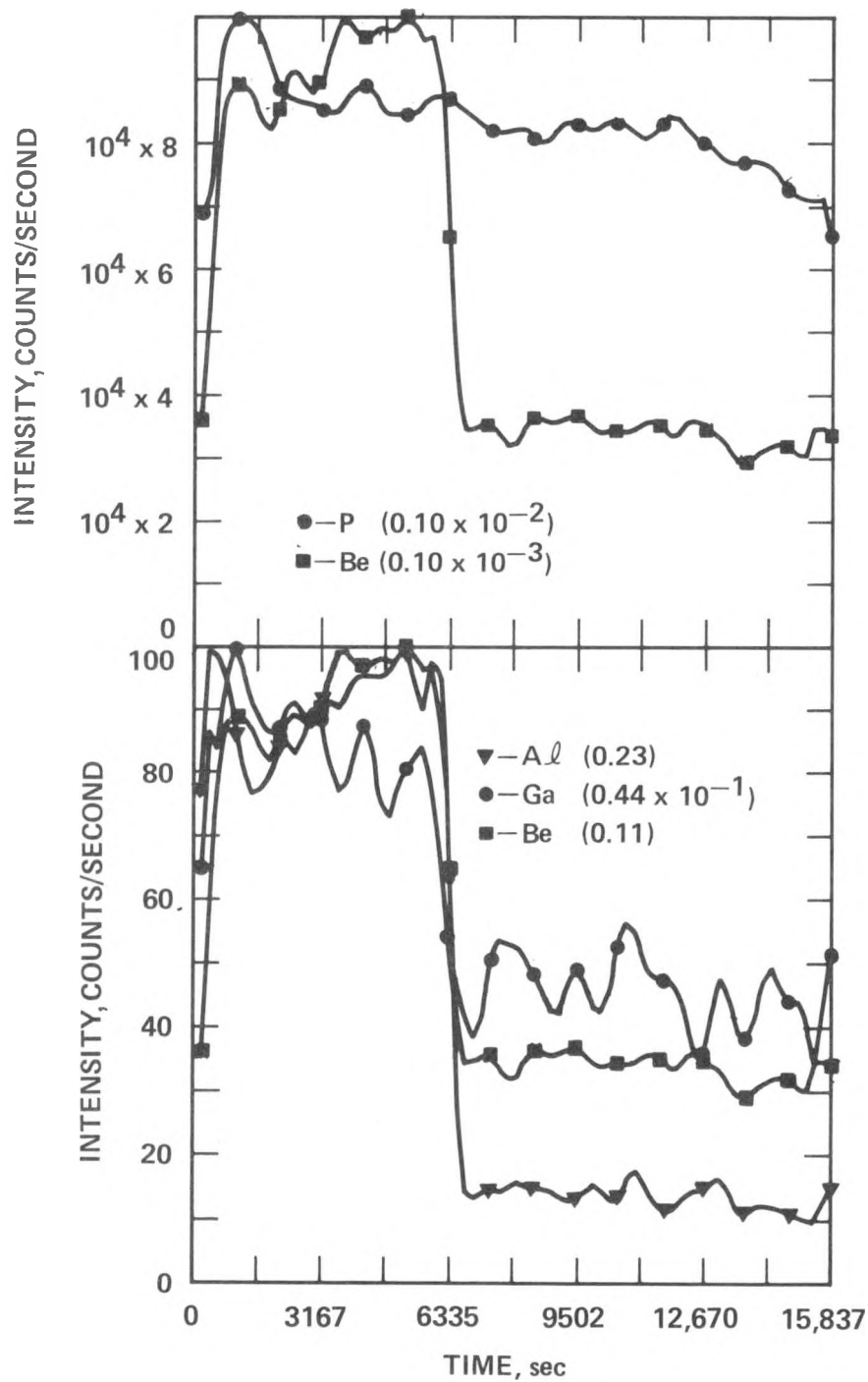


Figure 10. SIMS profiles n-InP/InP for InP Prepared at 300°C.

diffusion. For example, if we use $0.1\text{ }\mu\text{m}$ as the characteristic diffusion length for a one hour period at 300°C , we obtain an unusually high diffusion coefficient of about $10^{-14}\text{ cm}^2/\text{sec}$.

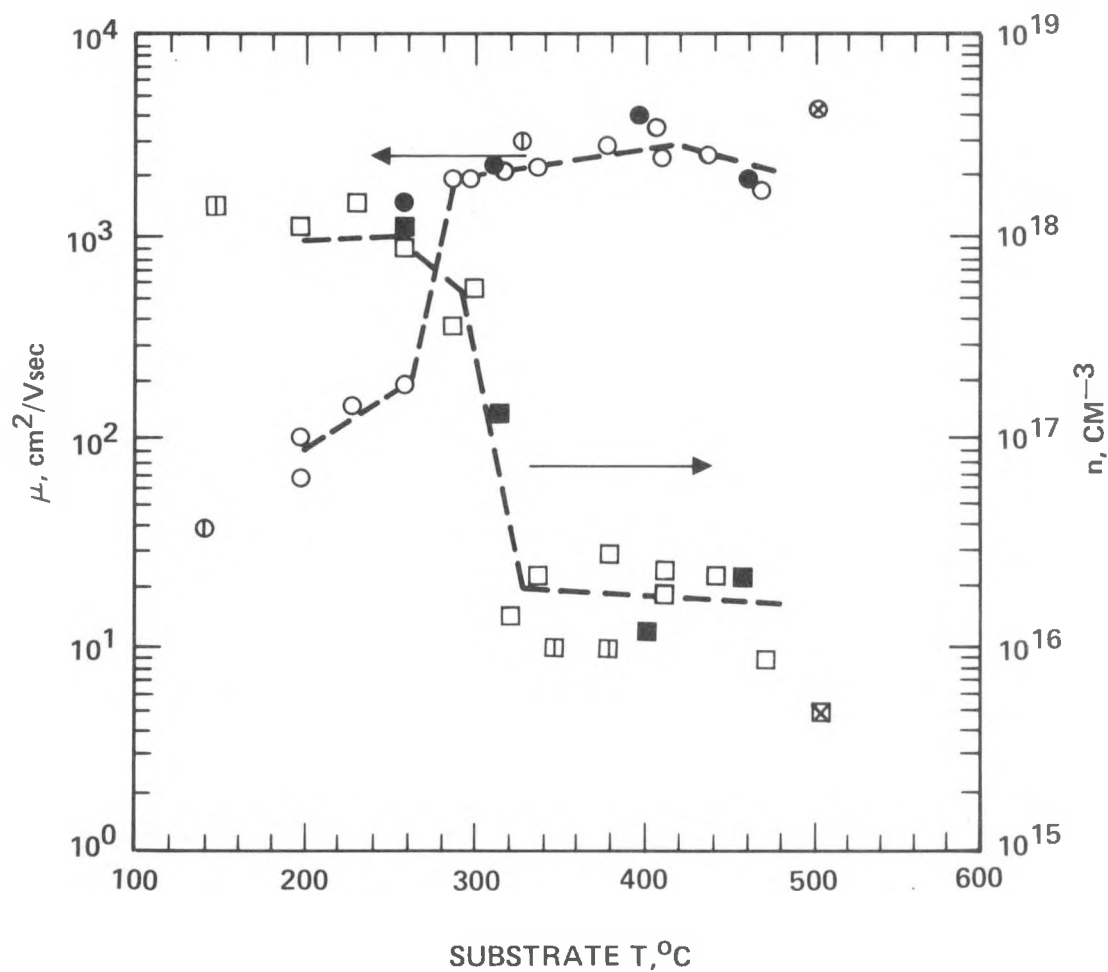
B. Zn DOPING

Zinc is a p-type dopant in InP and does not readily oxidize. As an alternative to avoid the transient doping effect with In sources containing Be/Al alloys, we have prepared p-type InP films by Zn doping. A small quartz cup (with a stem) is filled with Zn and then inserted in the PH_3 inlet line just below the source, as shown in Figure 11. The cup is positioned at a temperature so that the vapor pressure of its contents is sufficient to dope the InP film. We have prepared several p-type InP films by this technique on semi-insulating InP at a substrate temperature of about 380°C . Room-temperature carrier concentrations and hole mobilities of $6 \times 10^{16}\text{ cm}^{-3}$ and $80\text{ cm}^2/\text{Vsec}$, respectively, were achieved in the same film. Unfortunately, the concentration of unwanted defects in films prepared below a substrate temperature of 320°C is approximately 10^{18} cm^{-3} . This is much higher than the p-type doping levels required in our thin-films. Rather than pursuing further the p-type doping by Zn, it is necessary to first identify and reduce the concentration of these unwanted centers.

C. N-TYPE DOPING BY NATIVE DEFECTS OR IMPURITIES

It is difficult to determine whether either native defects or impurities are determining the electrical properties and preventing p-type doping below 320°C . There is a sharp change in the electrical properties of unintentionally doped n-type films^{2,3,4} at approximately 300°C . As the substrate temperature decreases (Figure 12), the mobility decreases. (We have plotted only our highest mobilities and the corresponding electron concentrations at these substrate temperatures.) Inversely, the electron concentration and concentration of electrically active centers increases with decreasing substrate temperature. The background impurity concentration for films prepared in different laboratories must be different. Certainly the background impurity

19



- ⊙ MOLECULAR BEAM EPITAXY (NORRIS REF. 2)
- ○ MOLECULAR BEAM EPITAXY (McFEE ET AL. REF. 3)
- ● PLANAR REACTIVE DEPOSITION
- ⊗ ⊗ LOW PRESSURE METAL ORGANIC CHEMICAL VAPOR DEPOSITION (DUCHEMIN ET AL REF. 4)

Figure 12. Unintentionally doped InP films prepared on InP substrates by vacuum technologies.

concentration of our system is higher when compared to the MBE systems. That the transition temperature from laboratory to laboratory is not strongly dependent upon temperatures suggests that the transition temperature is not directly related to background contamination, but associated with native defects.

MBE data² shows a change in the atomic morphology at 330°C and consequently, a possible change in the defect structure at that temperature. Above 320°C surface reconstruction was evident from RHEED patterns of InP deposited on (100) substrates. Below 320°C the surface were atomically smooth. If this transition in morphology also occurs in films prepared by PRD, we suggest the following to explain our electrical data. In the reconstructed surface shown in Figure 13, phosphorous is able to both evolve from and deposit on P sites which are located in the channels below the surface. Impurities such as carbon and oxygen readily diffuse via P vacancies. These impurity atoms are able to outgas from the system as H₂O, CO, and CH₄. However, at reduced temperatures the atomically smooth In layer reduces P migration, and buries impurities as they are deposited. Little diffusion and reaction with the vapor occurs. Although the increased electron concentration below 320°C may be due directly to trapped impurities, it may also be due to increased concentrations of nonequilibrium native defects.

If the electrical properties are dependent upon native defects they might vary with deviation from stoichiometry. The electrical properties were therefore examined as a function of $F_{\text{In}}/p_{\text{PH}_3}$ in unintentionally doped InP deposited on semi-insulating InP substrates. Here, F_{In} is the growth rate and p_{PH_3} is the PH₃ partial pressure. Figure 14 summarizes our data at 330°C. A value of 0.2 for $F_{\text{In}}/p_{\text{PH}_3}$ corresponds to growth near the In-rich boundary, since In droplets were present on our films grown under these conditions. At higher $F_{\text{In}}/p_{\text{PH}_3}$, and within the single phase region, we found the electron concentration to vary from 6×10^{17} to $4 \times 10^{18} \text{ cm}^{-3}$ with no dependence of electron concentration on $F_{\text{In}}/p_{\text{PH}_3}$. For a more ionic semiconductor, such as CdTe, material should become more n-type with increasing $F_{\text{In}}/p_{\text{PH}_3}$. Such a behavior might be due to an excess of anion vacancies acting as donors.

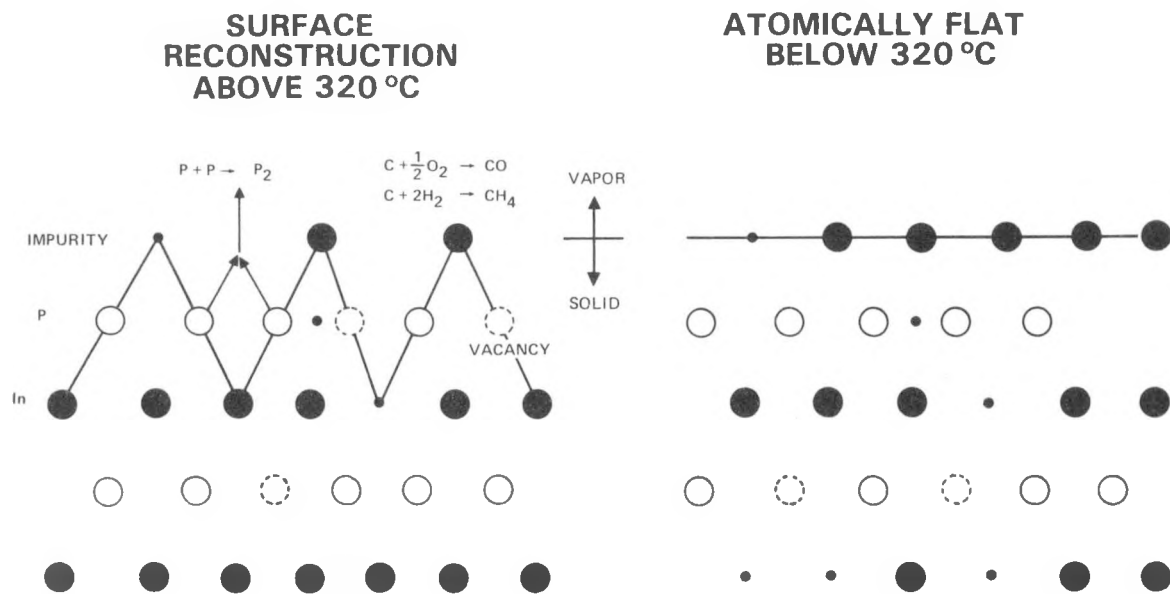


Figure 13. InP surface structure (left) above 320°C with surface reconstruction and (right) below 320°C without surface reconstruction.

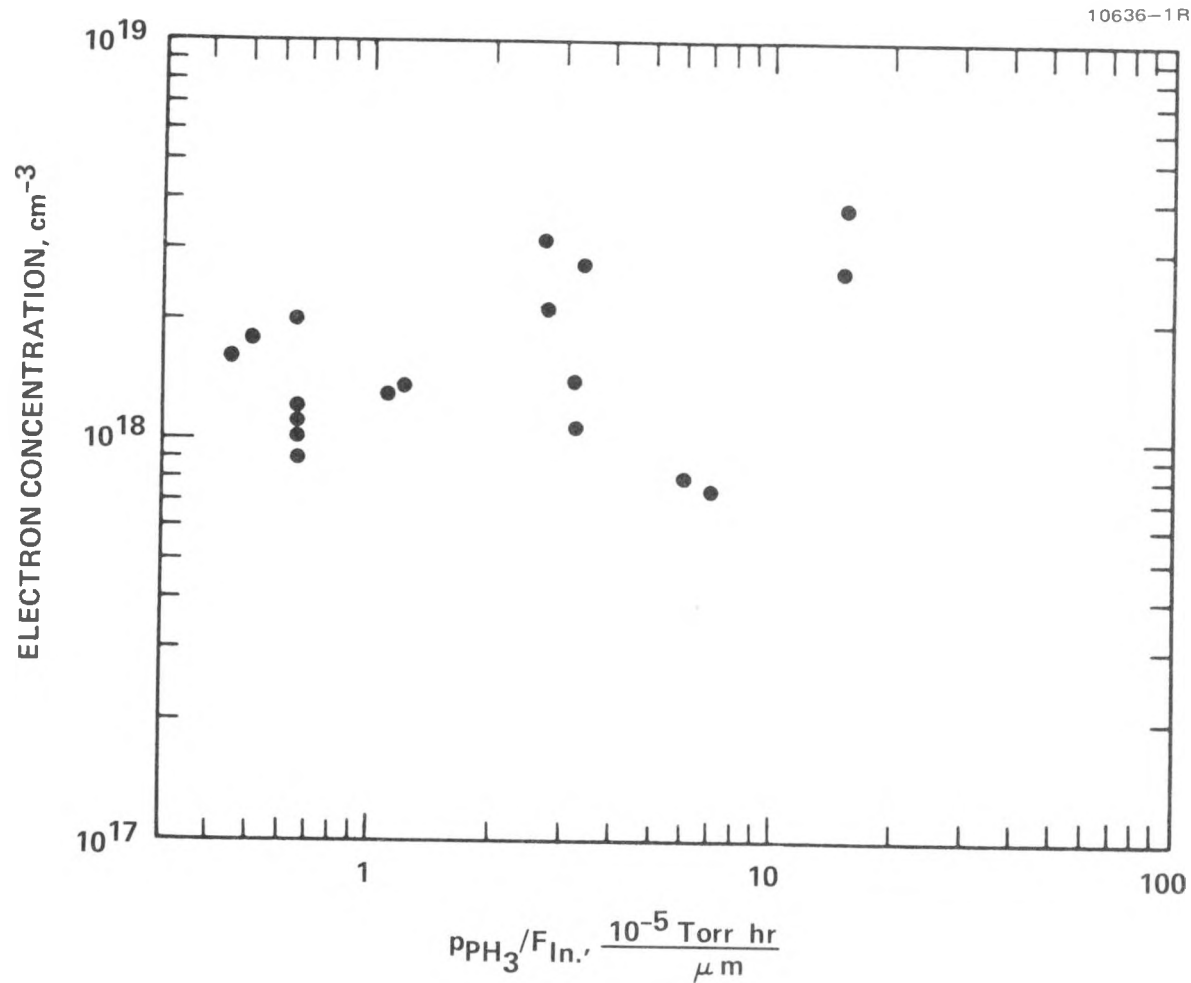


Figure 14. Electron concentration of undoped InP prepared at 330°C versus the ratio of the reactants.

For more covalent material, such as GaAs, material should become more p-type, with an increasing anion to cation mole fraction ratio in the vapor phase. Such a behavior in GaAs has been associated with amphoteric Group IV impurities occupying Group V anion sites and acting as acceptors. The sharp transition in electrical properties with substrate temperature suggests that native defects dominate the electrical properties at about 300°C. However, the independence of the electrical conductivity on deviations from stoichiometry suggest that the electrical properties are not related to native defects. A clearer picture is presented if we consider native defects introduced by nonequilibrium processes. Obviously, the equilibrium concentration of native defects is several orders of magnitude less than 10^{18} cm^{-3} . If native defects are introduced, they then must be present in unequilibrium concentrations and not follow the laws of mass action.

D. ANALYSES FOR IMPURITIES

Several studies were initiated to determine the impurity content of these films. In the SIMS analyses of the films, only Al, Be, and Ga were found. The background concentration levels for the common n-type impurities are likely to be below 10^{17} cm^{-3} . The system was not sensitive enough to detect carbon using the oxygen beam as the sputtering source. Therefore, if oxygen was present and carbon acts as an amphoteric impurity, n-type impurities may be present, but the level of n-type impurities could not be established. In another InP thin-film program at HRL, films were deposited on Si substrates by PRD at 400°C and analyzed by spark spectrographic analysis. Carbon and oxygen were detected in concentrations of less than 10^{17} cm^{-3} . However, lower concentrations of impurities are possible, due to favorable surface kinetics at elevated temperatures.

Additional experiments were undertaken to identify and reduce the background impurities in our system. The indium source was examined by SIMS, the source/substrate was changed and cleaned several times, and the quality of the vacuum was improved.

Figure 15 shows a SIMS analysis of an undoped In source by Charles Evans & Associates using an oxygen beam. A mass spectrum (from mass 1 to 250) was obtained from the surface region and from the bulk of a high-purity In foil. The relative ion intensities between the two In samples are different because of extraction efficiencies resulting from changes in sample topography. For example, the ^{115}In intensity, which was measured with a Faraday cup, is 6.0×10^6 for the In foil and 6.0×10^5 for the In source. The Faraday cup was inserted into the secondary ion beam for ^{113}In through ^{115}In because the In^+ signal was too intense to be placed on the electron multiplier. The intensity measured by the Faraday cup needs to be multiplied by 1200 to be on the same scale as the remaining ions, which were measured on the electron multiplier. When comparing impurity ion intensities between the two In samples, the ratio of the impurity intensity to the In matrix ion intensity should be used. The impurities, which were found to be more abundant in the In source than in the In foil, are ^9Be , ^{27}Al , ^{40}Ca , ^{56}Fe , and ^{69}Ga . Increased concentrations of C were not found. A depth profile (Figure 16) of ^9Be , ^{27}Al , ^{40}Ca , ^{56}Fe , and ^{69}Ga in the In source was then made. The abrupt change in ion intensity four-fifths of the way through the profile resulted when the sputtering rate was increased four-fold. Each element shows a gradual decrease in intensity versus depth. Surprisingly, the SIMS shows high levels of Be and Al in the undoped source. This is thought to be due to Al and Be in the residual In located in the PH_3 inlet line, and which subsequently doped the new source. Regardless, this level of Be does not dope the p-type films. The InP prepared with this source was n-type.

After Al and Be were found in our In source we cleaned the system and the inlet lines. The source/substrate assembly and the indium source were again replaced. A decrease in the carrier concentration at these low substrate temperatures was not found after these changes were made.

While these changes were made we also reduced the background pressure of the system. Figure 17 shows RGA spectra (a) during pumpdown after sample loading, (b) before filling with LN_2 , (c) after adding LN_2 to the shroud, (d) while throttling the gate valve to increase the background pressure of noncondensable gases, (e) during source out-gassing, and (f) four hours after

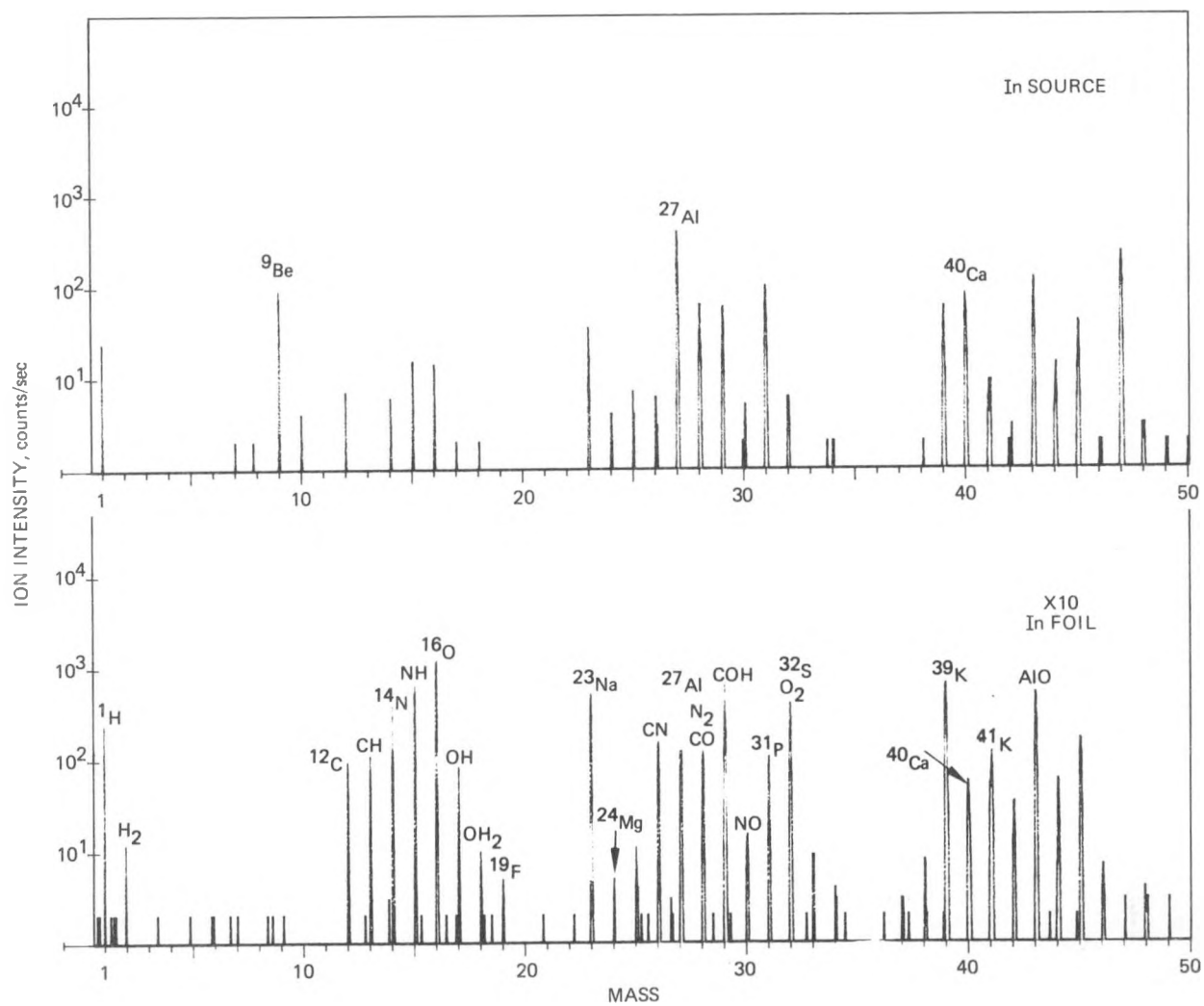


Figure 15a. SIMS analysis of surface of In source and pure In foil for mass 1 through 50.

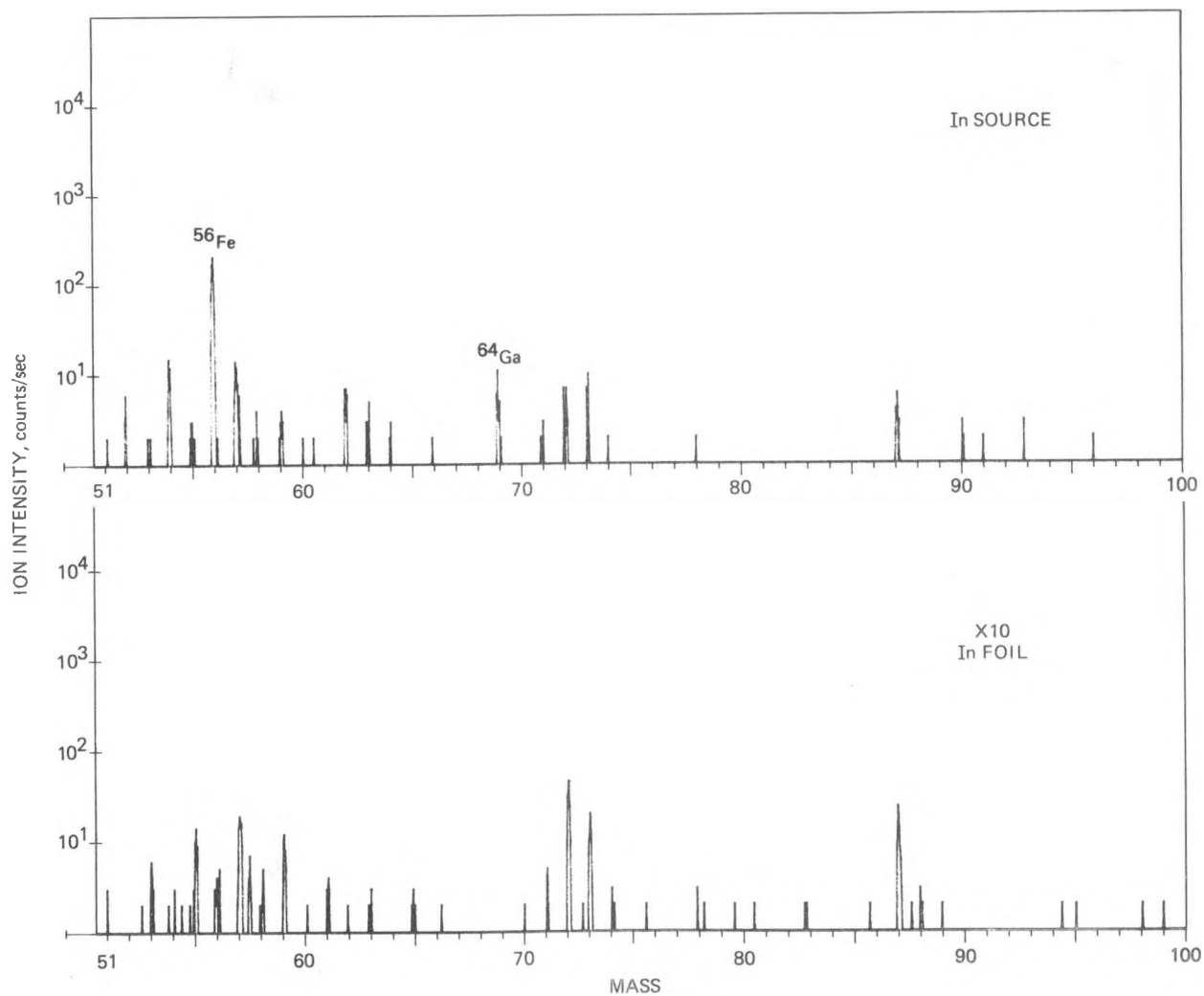


Figure 15b. SIMS analysis of surface of In source and pure In foil for mass 51 through 100.

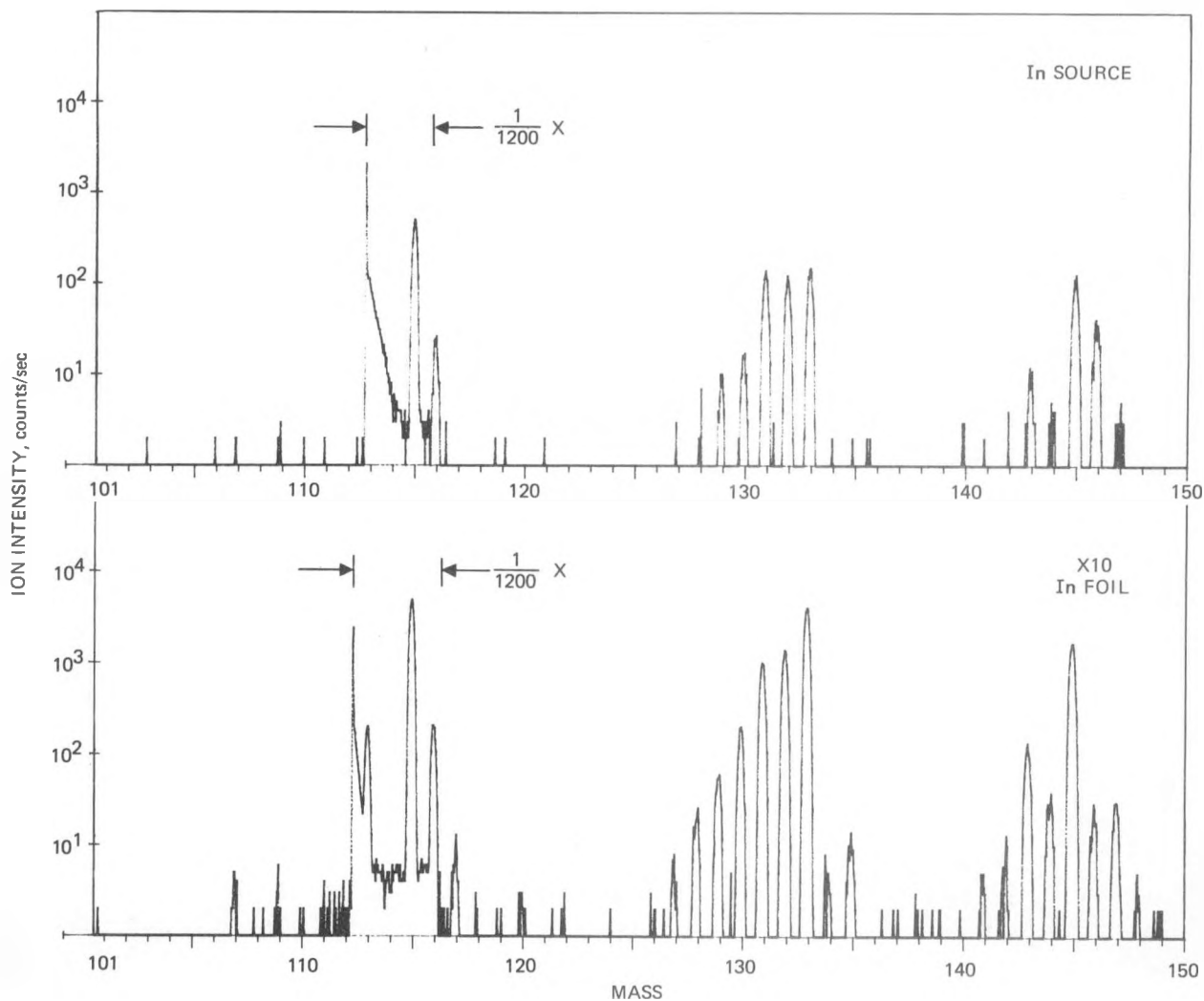


Figure 15c. SIMS analysis of surface on In source and pure In foil for mass 101 through 150.

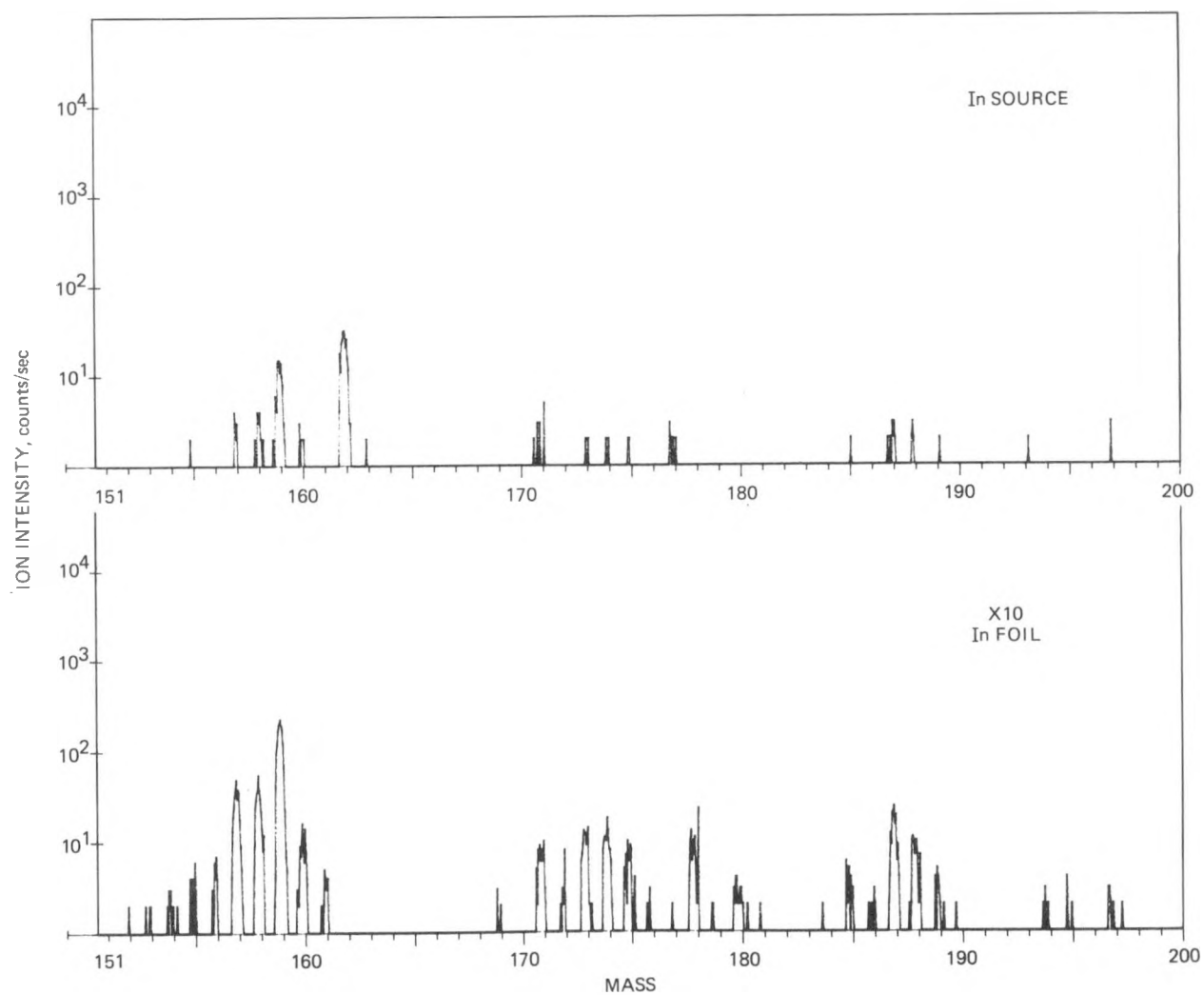


Figure 15d. SIMS analysis of surface of In source and pure In foil for mass 151 through 200.

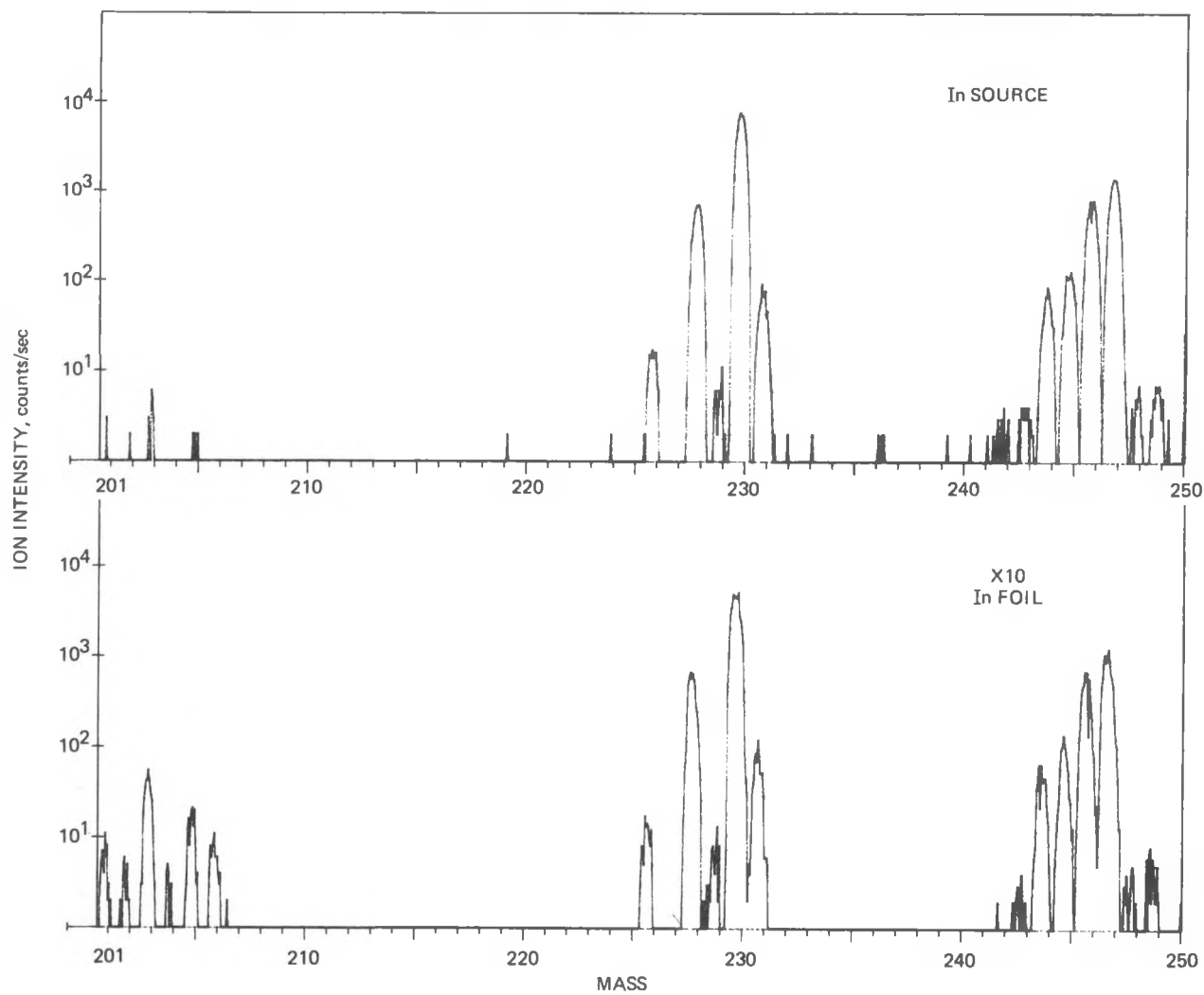


Figure 15e. SIMS analysis of surface of In source and pure In foil for mass 201 through 250.

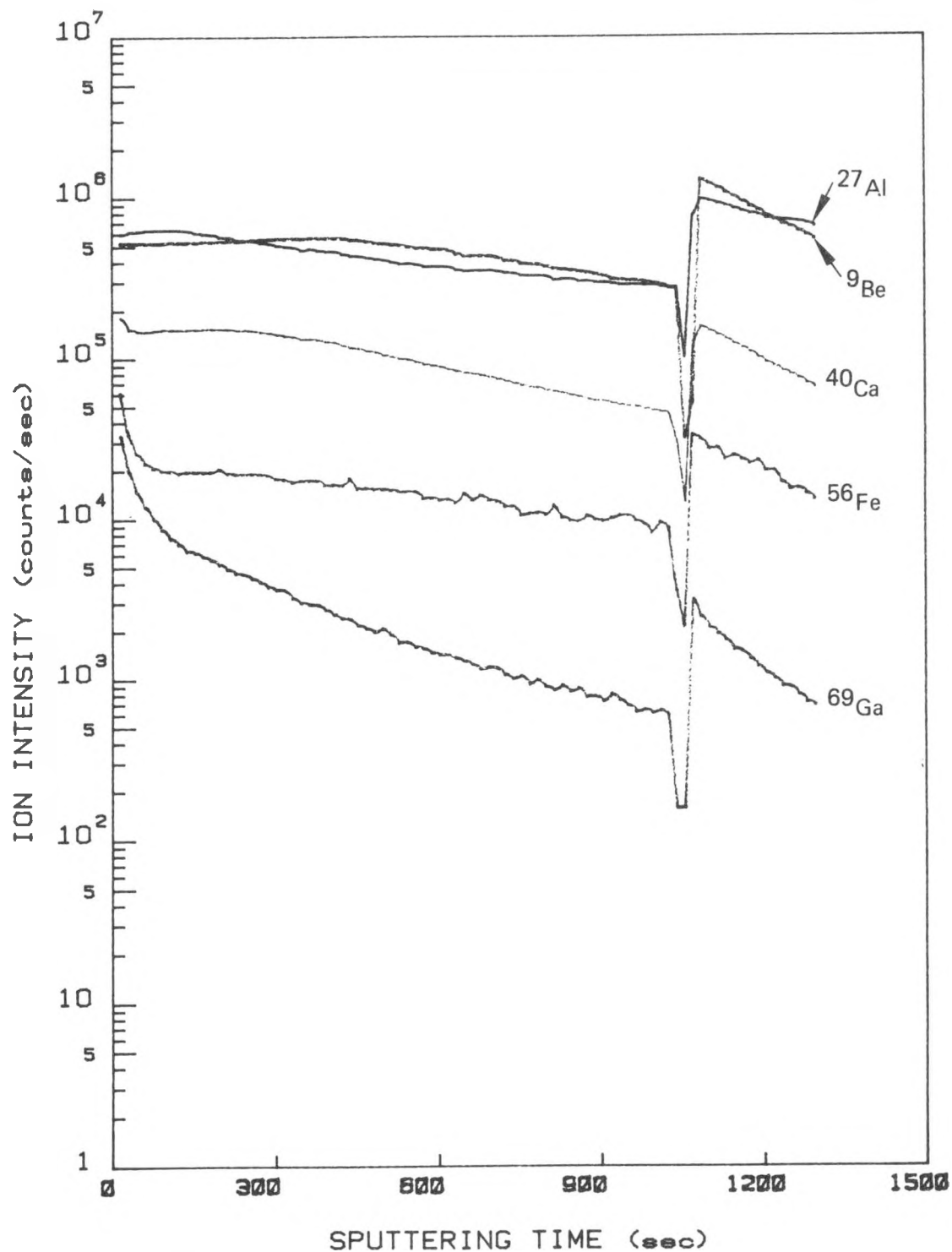


Figure 16. SIMS depth profile of ^9Be , ^{27}Al , ^{40}Ca , ^{56}Fe and ^{69}Ga in In source.

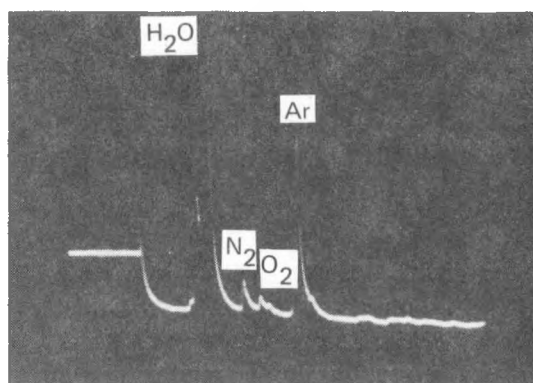
the run. After loading and pumping down the system, the total pressure was about 10^{-7} Torr, due to water vapor. Normally, the N_2 and O_2 doublets in Figure 17(a) (characteristic of air) are observed after pumpdown in (b) and (c). The doublets were not present after the vacuum was improved. This corresponded to at least a factor of 3 decrease in the partial pressure of O_2 and N_2 . Even though the partial pressure of O_2 was reduced, there was no decrease in the electron concentration. To help identify our background contaminants we throttled the gate valve while the shrouds were filled with LN_2 . The intensities of the CO peak and another unknown peak corresponding to a higher mass increased. The gate valve was then fully opened and the spectrum was again characteristic of Figure 17(c). During the outgassing the pressure rises as a result of the release of H_2 and CO from the source. (The horizontal and vertical gains for RGA spectra (a) through (c) were not all the same. Therefore, it could be misleading to associate the partial pressure with areas under the peaks.) The CO is also released into the deposition chamber during growth. We suspect C as being the most likely foreign impurity to affect our electrical properties since we saw no effect of oxygen on our electrical properties.

Alternatives to solving the p-type doping problem include: 1) Preparing InP on $RxCdS$ above $320^\circ C$ where p-type doping can be obtained. This will be discussed in Section 3.E. 2) Preparing InP below $320^\circ C$, but in an environment which will alter the surface kinetics. This will be discussed in Section 3.F. 3) Preparing alternative InP/ $RxCdS$ device structures. This will be discussed in Section 4.

E. InP EPITAXY ON $RxCdS$

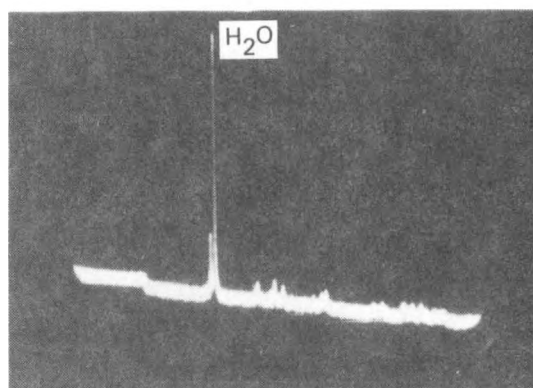
In our study of the epitaxy of InP on $RxCdS$ the substrate configuration is similar to the configuration that would be used in all of the thin-film devices. Figure 18 is a SEM picture of an InP film deposited on a $RxCdS$ /ITO/GLASS structure. There are two ITO regions. The ITO at the peripheral

10642-7



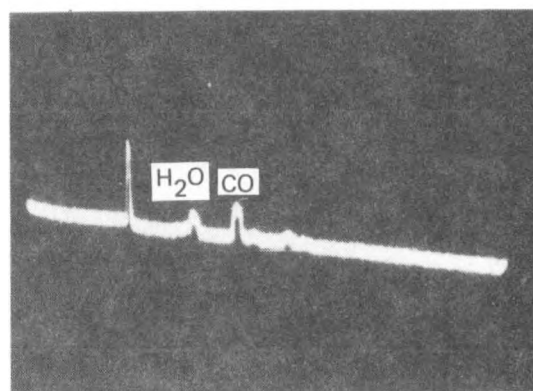
(a) 1×10^{-6} Torr
DURING PUMPDOWN

10642-8



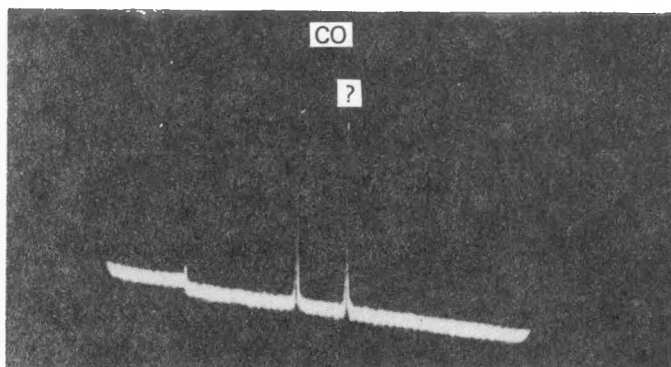
(b) 9×10^{-8} Torr
BACKGROUND, No LN_2

10642-9



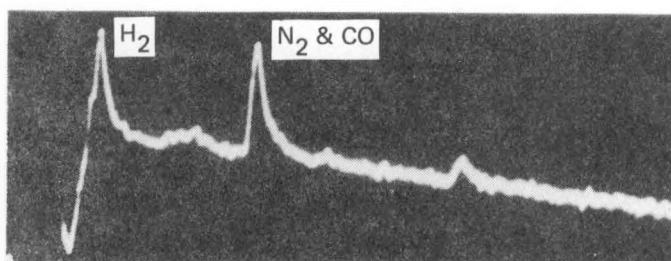
(c) 9×10^{-9} Torr
BACKGROUND, WITH LN_2

Figure 17. Residual gas spectra outside LN_2 shrouds. (a) During pumpdown after sample loading. (b) Before filling with LN_2 . (c) After filling with LN_2 . (Sheet 1 of 2)



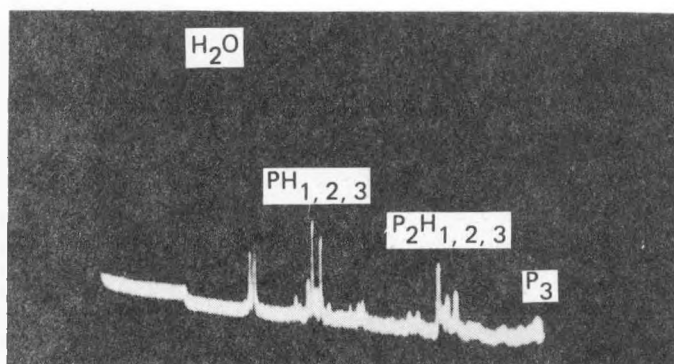
10642-10

- (d) 3×10^{-7} Torr
BACKGROUND, WITH LN_2 AND
GATE VALVE THROTTLED



10642-11

- (e) 7×10^{-8} Torr
DURING SOURCE
OUTGASSING



10642-12

- (f) 1.5×10^{-7} Torr
4 HOURS AFTER RUN

Figure 17. Residual gas spectra outside LN_2 shrouds. (d) After filling with LN_2 and throttling gate valve. (e) During source outgassing. (f) Four hours after run. (Sheet 2 of 2)

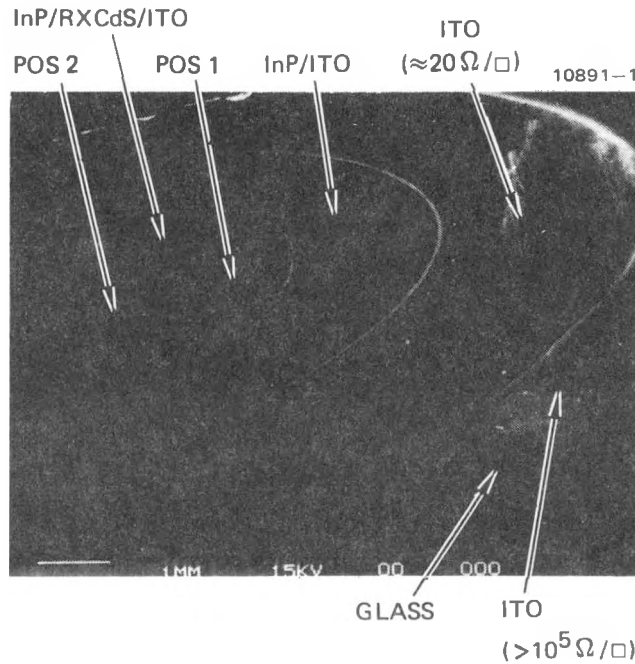


Figure 18. Scanning electron microscope picture of InP/RXCdS/ITO/GLASS structure.

region has a sheet resistance greater than $10^5 \Omega/\square$ because it was exposed to the H_2S during the recrystallization of the CdS at high temperatures. After the recrystallization process, an outer ring of RXCdS was removed by etching, leaving an RXCdS mesa surrounded by low sheet resistance, ITO ($\approx 20 \Omega/\square$). The diameter of the InP deposition is intentionally larger than the RXCdS mesa to cap the RXCdS to prevent S-doping via vapor transport.

We prepared films of InP on RXCdS at different substrate temperatures. Figure 19 shows SEM and corresponding x-ray Read pictures of from one- to 5- μm -thick InP films prepared on RXCdS at 280°C, 330°C, and 380°C. The best results at 280°C show grain boundaries and faceting of the grains. In the SEM picture the artist has delineated the grain boundary. Across this grain boundary there is a definite difference between the orientation of the facets. The corresponding x-ray picture is dominated by spots rather than rings, which is characteristic of grains having large, rather than submicron, lateral dimensions. Out of five runs at 280°C only two resulted in the epitaxy of

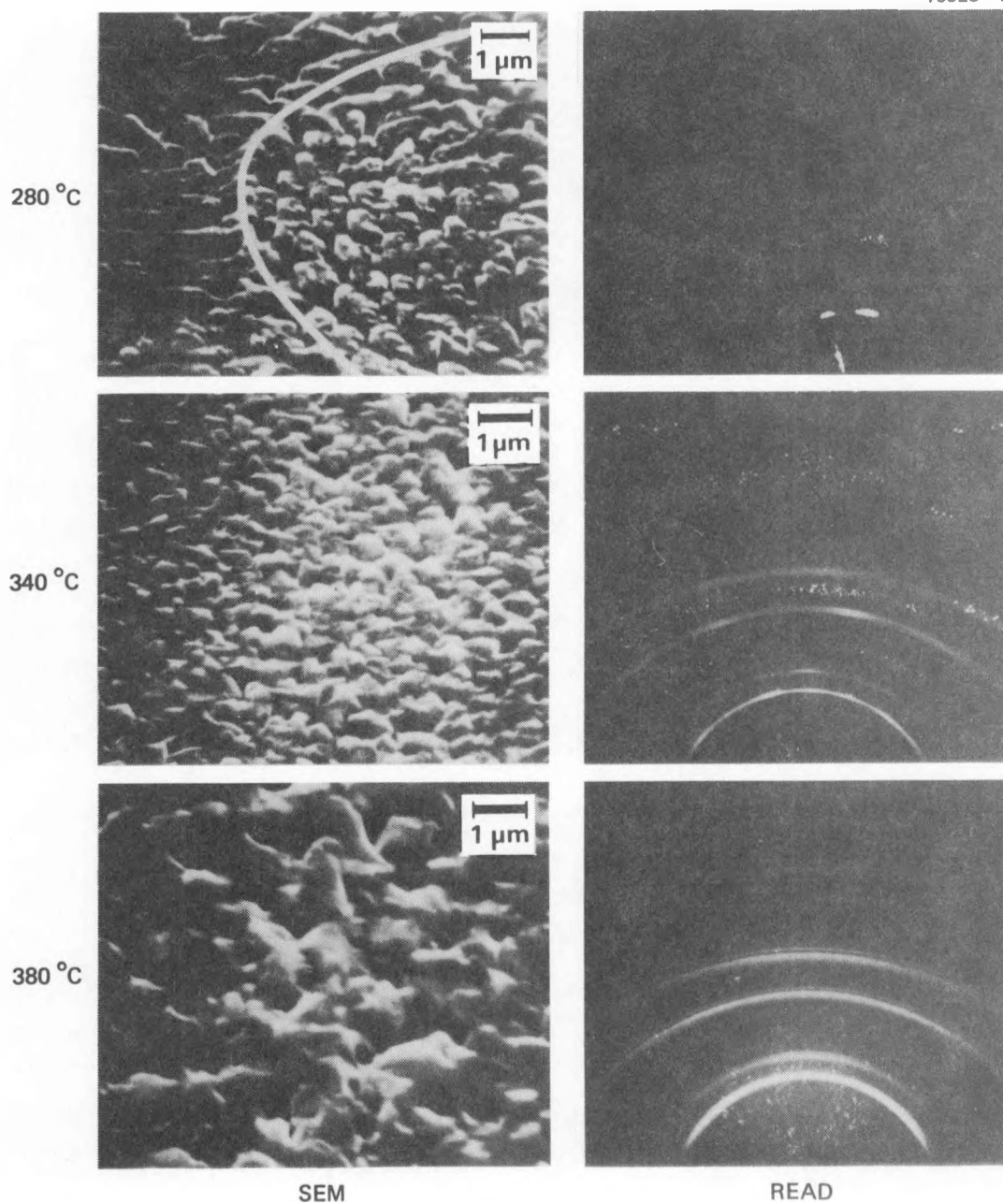


Figure 19. SEM and x-ray Read pictures of InP deposited on RXCdS at different substrate temperatures.

InP on RXCdS. Figure 20 shows higher magnification SEM pictures of a 0.15- μm -thick film deposited at 280°C on (top) the ITO/GLASS substrate, (middle) the RXCdS at Position 1 in Figure 19, and (bottom) the RXCdS at Position 2 in Figure 19. The InP deposited on the ITO/GLASS is polycrystalline. The InP deposited at the peripheral region of the RXCdS mesa shows a uniform distribution of the platelets and whiskers. The composition and cause of the whiskers is presently unknown. About 70 percent of the InP deposited at the interior of the RXCdS shows aligned facets which indicate that the InP replicates the crystal structure of the RXCdS substrate grains. The epitaxial deposition of InP on RXCdS is not understood. There is no apparent reason why either epitaxy did not occur at the peripheral of the RXCdS, or why it was not consistently achieved in other runs.

At the center of the InP/RXCdS/ITO structure there appeared to be good coverage of the InP. However, in isolated regions the facets appeared to grow more vertically from the RXCdS substrate and appear to leave the RXCdS exposed. The RXCdS grains in these regions are of an orientation which is significantly different than the rest of the grains. We examined these regions in more detail. Figure 21 (top) shows the boundary between two grains, one of them having more vertical growth. The morphology of the grain on the left side is typical of the coverage in the interior of the RXCdS mesa. The morphology of the grain on the right side represents the grain with more vertical growth. This SEM picture, and those in Figure 20, were taken at 45°, with respect to the plane of the film. When SEM pictures were taken at even more normal orientation the coverage appeared to be more complete. For example, a picture of the same region at 65°, as in Figure 21 (bottom), shows more uniform coverage. There also does not appear to be complete coverage of the InP where poor epitaxy was achieved at the peripheral of the RXCdS mesa, as in Figure 20 (middle). Here the surface appears to be decorated with platelets and whiskers. In order to qualitatively assess the extent of the InP coverage, we used the microprobe to examine grains having 1) apparent complete coverage, as in Figure 20 (bottom), 2) vertical epitaxial growth, as in the right side of Figure 21 (top), and 3) poor epitaxy, as in Figure 20 (middle). Unfortunately, the 30 keV beam is capable of penetrating through

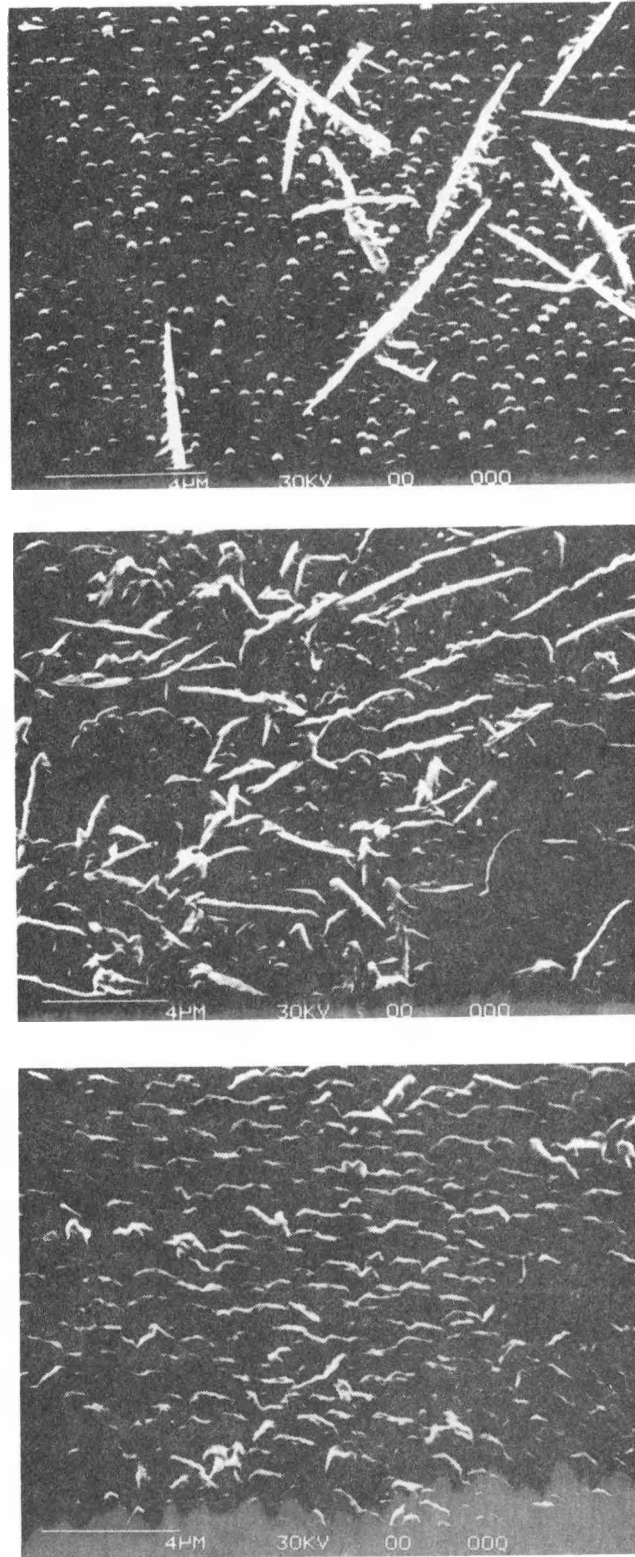


Figure 20. Scanning electron microscope picture of InP deposited on (top) the ITO/GLASS substrate, (middle) the outside of the RXCdS mesa and (bottom) the interior of the RXCdS mesa.

10891-2

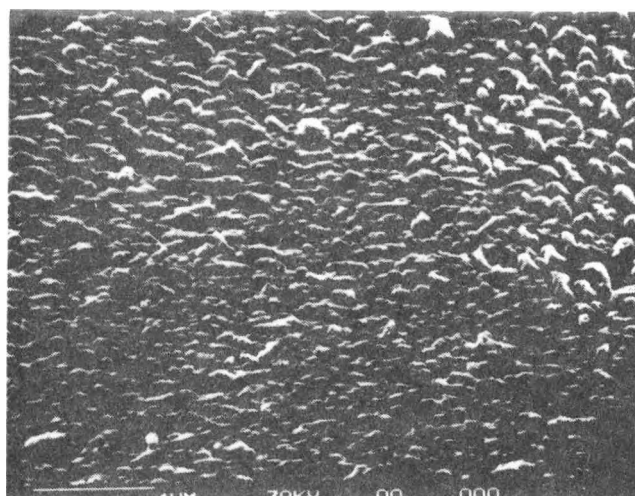
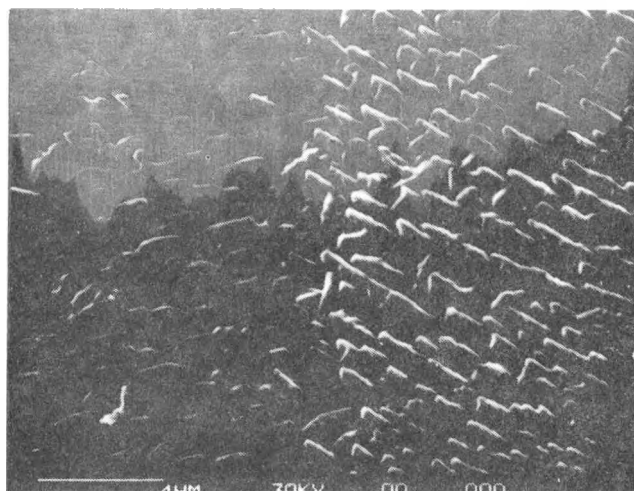


Figure 21. Scanning electron microscope picture of two grains of InP at (top) 45° with respect to the plane of the film and (bottom) 65° with respect to the plane of the film.

our InP film, which would result in a sulfur peak even though complete coverage occurs. The beam energy was reduced to reduce the degree of penetration. When the structures were scanned there was no difference in the In to S ratio. The reverse current characteristics of p-InP/RXCdS thin-film diodes also suggests good coverage of the p-InP. (See final report to DoE, XJ-8170-1). At a reverse bias of 0.2 V the contribution of the reverse current due to pinholes is less than 1 mA/cm^2 . The microprobe study suggests that the degree of coverage in the regions in question is better than expected from the SEM photographs. However, Auger studies must be undertaken to examine the degree of coverage in more detail.

SEM pictures of films prepared at 380°C (Figure 19, bottom) show neither faceting nor grain boundaries. The x-ray Read picture is documented by rings rather than by spots characteristic of submicron size grains. Films prepared at 330°C (Figure 19, middle) are of intermediate quality. The SEM shows faceting, but the facets are not oriented, and the grain boundaries are not evident. Nucleation and growth of numerous crystallites with orientations other than that of the RXCdS are occurring. It is not clear whether extraneous nucleation is a result of either a contaminated RXCdS surface, severe deviations from stoichiometric CdS, or a transition region.

We undertook studies to determine the composition of the transition region. In earlier studies of InP prepared on CdS at about 425°C we found an In-Cd-S transition region⁶ about $1\text{-}\mu\text{m}$ -thick between the InP and the CdS. The measurements at 425°C were made by scanning cleaved structures with a microprobe. Hanford Engineering Development Laboratory (HEDL) has also undertaken SIMS profiles⁷ of InP/RXCdS structures. Figure 22 shows SIMS profiles for In, Cd, P, S, Be, and Al of a $4.6\text{-}\mu\text{m}$ -thick Be-doped film deposited on RXCdS at 380°C .

The interface is clearly defined, and the Cd, S, Al, and Be profiles are well behaved. The ^{115}In profile shows a peak at the interface. HEDL interprets this peak to be an artifact of the ionization process caused by enhancement by sulfur. To check this interpretation, HEDL profiled $^{147}\text{InO}_2$ and found a reduced count rate. Comparison of the ^{115}In and $^{147}\text{InO}_2$ profiles supported the thesis that the increased ^{115}In and reduced $^{147}\text{InO}_2$ count rates

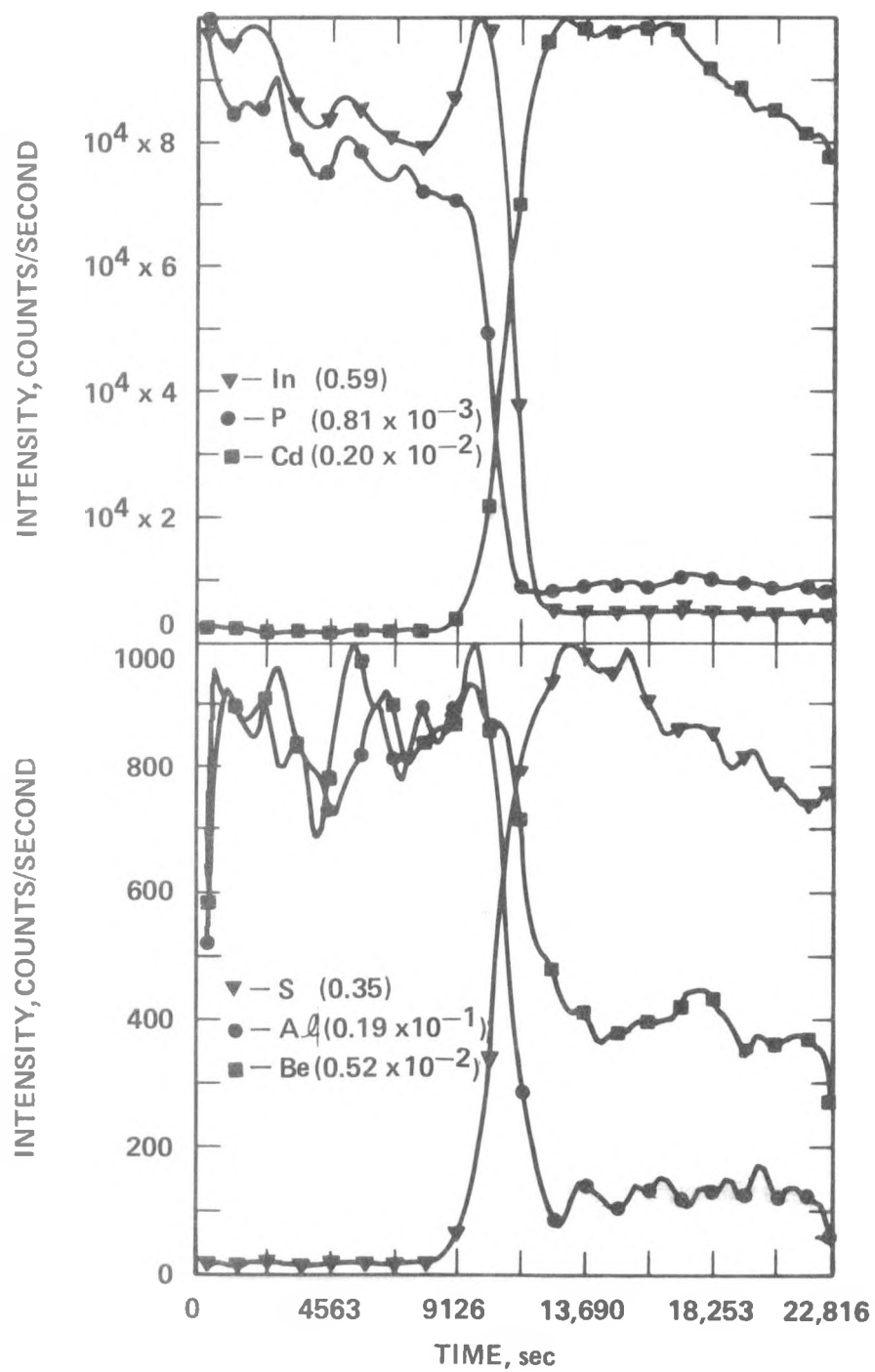


Figure 22. SIMS profiles p-InP/RXCdS for InP deposited at 380°C.

were ionization artifacts. Further details of these studies are found in the HEDL report⁷. The P profile suggests P depletion at the interface. This would be consistent with earlier SEM studies for films prepared at 420°C which indicated P depletion at the interface. However, we feel that this also is an artifact of the ionization process; first, because SIMS analysis indicates the depletion to extend about 1 μm from the interface (this is about an order of magnitude wider than we determined by optical studies, which we will discuss later), and second, because the degree of depletion does not decrease with a decrease in the substrate temperature.

Figure 23 shows profiles for In, Cd, P, and Al for an undoped n-type 2- μm -thick InP film deposited on RXCdS at 330°C. There was no significant difference in the In, P, and Cd profiles between substrate temperatures of 330 and 380°C corresponding to profiles in Figures 22 and 23, respectively. Although a Be/Al alloy was not incorporated in the source, SIMS analysis found Al, which was distributed locally at the InP/CdS interface. We obtained good epitaxial growth of InP on RXCdS at lower substrate temperatures using intentional Be/Al doping. As discussed earlier, SIMS of unintentionally doped InP films show that Be and Al can be incorporated from residual In, located in the PH_3 inlet tube, from an earlier run.

There is not a significant difference between the slopes of the profiles at the interface for structures prepared at 330 and 380°C. Effects of diffusion on the profiles are masked by system resolution ($\pm 0.5 \mu\text{m}$) at this sputtering rate. These SIMS profiles show that severe interdiffusion between InP and CdS over distances greater than a micron does not occur. Actually the degree of interdiffusion at 380°C is a few tenths of a micron. This was determined by simultaneously depositing InP films of this thickness on RXCdS, InP, and glass. When InP films deposited on glass were examined in transmission to visible light, they were not completely opaque. Detailed measurements of films on InP and glass confirmed thicknesses on the order of a few tenths of a micron. It was not apparent that InP was deposited on the RXCdS. Instead, a yellow deposit having approximately the same bandgap of CdS was found. Microprobe measurements indicated that only In was deposited and the yellow film was InCdS. Below substrate temperatures of 300°C the transition layer is much

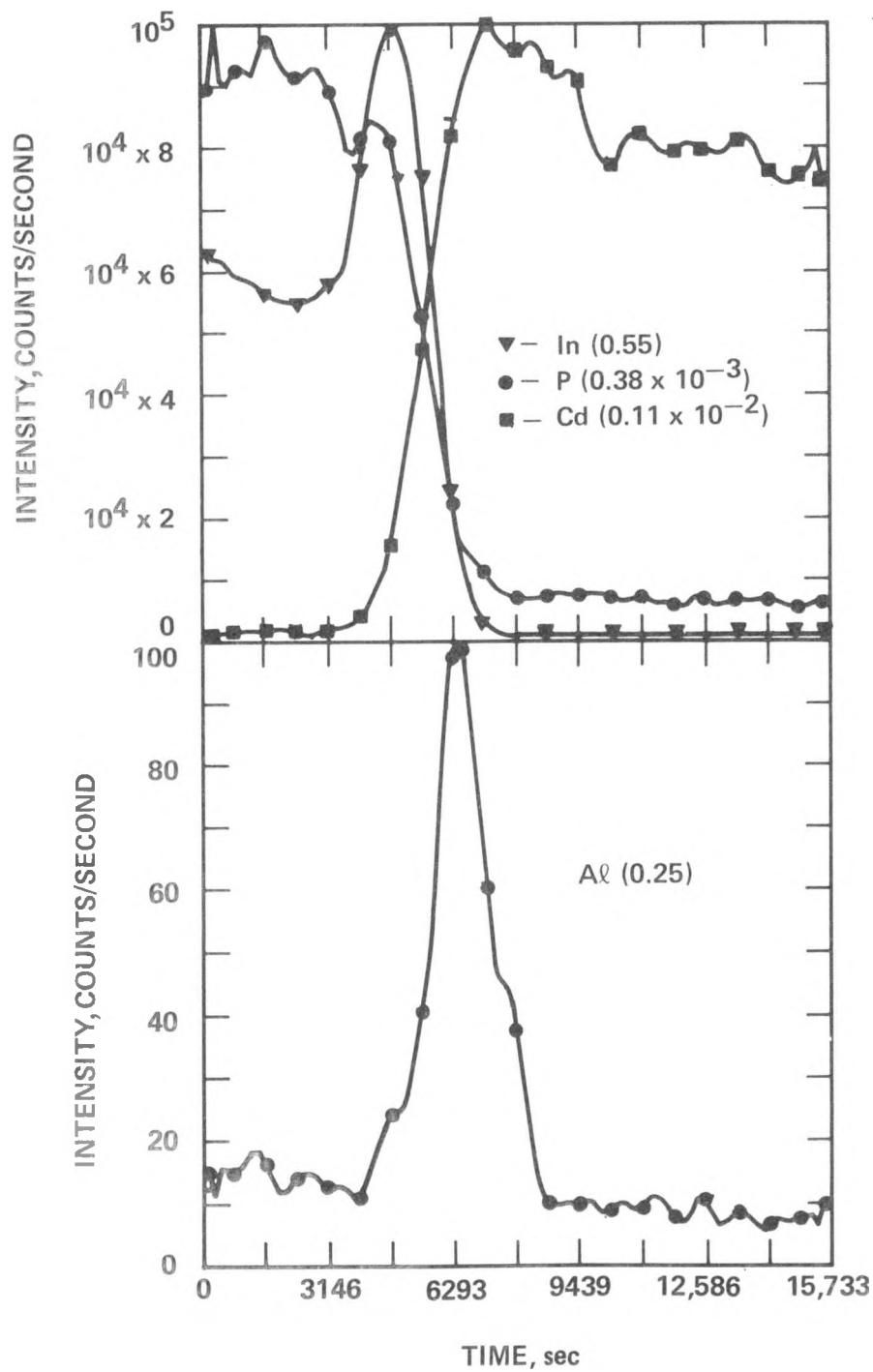


Figure 23. SIMS profiles n-InP/RXCdS for InP prepared at 330°C.

less than 1,000 Å thick. Transmission electron microscope measurements of 100 Å thick films of InP prepared on CdS at 300°C confirm this and show no transition region⁸.

F. InP GROWTH WITH HALIDES

In order to realize a thin-film cell, it is more promising to achieve p-type doping below 320°C where epitaxy of InP on RXCdS has already been demonstrated than to attempt to achieve epitaxy above 320°C, even though p-type doping has already been demonstrated. The formation of only a few atomic layers of InCdS at the InP/RXCdS interface may hinder good InP epitaxy. Even if epitaxy could be demonstrated above 320°C, unforeseen interdiffusion problems, especially at grain boundaries, might complicate further development of an all thin-film cell.

If impurities are controlling the electrical properties below 320°C, then it is desirable to prevent them from being incorporated in the lattice. Two approaches are to 1) reduce the source of impurities, and 2) incorporate the impurities into volatile compounds. The growth of InP films in a fused silica reactor under vacuum conditions is an attractive method of reducing the background concentration of impurities, including carbon. Fused silica is an acceptable material for the growth of high purity films. For example, Calawa⁹ grew high purity GaAs by modified MBE in a fused silica reactor.

As an approach to form volatile compounds containing impurities, we use H₂ in our PRD system. Carbon and O is intended to react with H₂ to form H₂O and CO. We do not have evidence to substantiate this, but the room temperature mobility of our best InP films is better than the mobility of InP film prepared by MBE. Evidence to support our approach is provided by Calawa. When Calawa introduced As in the form of AsH₃ to form GaAs by MBE he obtained the purest GaAs films prepared by MBE.

The highest purity thin-films of III-V compounds are produced by chemical vapor deposition using halide transport. An additional step to form volatile compounds containing impurities might be to combine halide chemistry with vacuum growth. With the help of internal funding we have assembled a CVD system which is capable of operating at either atmosphere or

reduced pressure. Figure 24 shows the gas manifold, PCl_3 bubbler, and fused silica reactor. When the system is operating at reduced pressure the gases are exhausted through either the forepump or the turbopump. A schematic of the reactor is shown in Figure 25. The reactor is meant to eventually replace the PRD source/substrate assembly and is intended to be incorporated in the metal vacuum chamber. Operation in the metal vacuum chamber will permit the substrate plate to be rotated over the source. Undertaking preliminary experiments outside the metal vacuum chamber allows the growth conditions to be optimized more readily and allows the degree of corrosive action of the halides on metal parts to be assessed.

When PCl_3 is introduced into the reactor it decomposes in the crucible containing In to form P_4 and Cl_2 . The partial pressures of HCl , In, InCl , P_4 , H_2 , and Cl_2 depend upon the total pressure, pumping speed, and the PCl_3/H_2 ratio. In, InCl , and P_4 are deposited on the substrate to form InP . Among many other differences, this process is different from PRD in that Cl is incorporated at the InP surface. Indium on the surface in the form of volatile InCl should alter the surface kinetics and may lower the transition temperature from a reconstructed to atomically smooth surface. The presence of a reconstructed surface would then allow impurities to diffuse via the channels. At the surface, Cl might getter impurities, especially Group IV impurities, to form volatile group IV chlorides. We have grown films of InP on (100) InP at 600°C and at atmospheric pressure. The next step is to grow films at reduced pressures and temperatures.

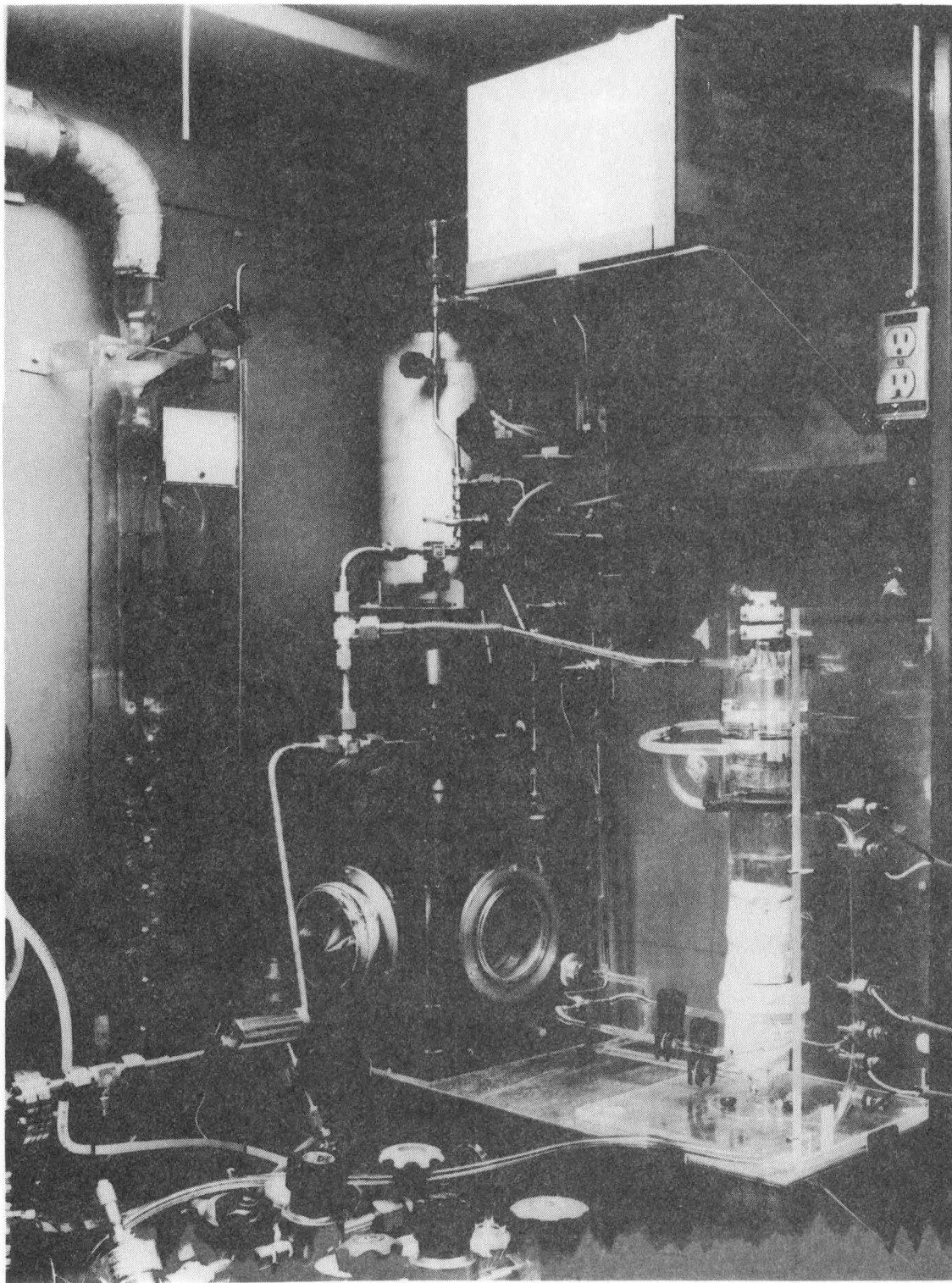


Figure 24. Low pressure InP/PCl₃ system.

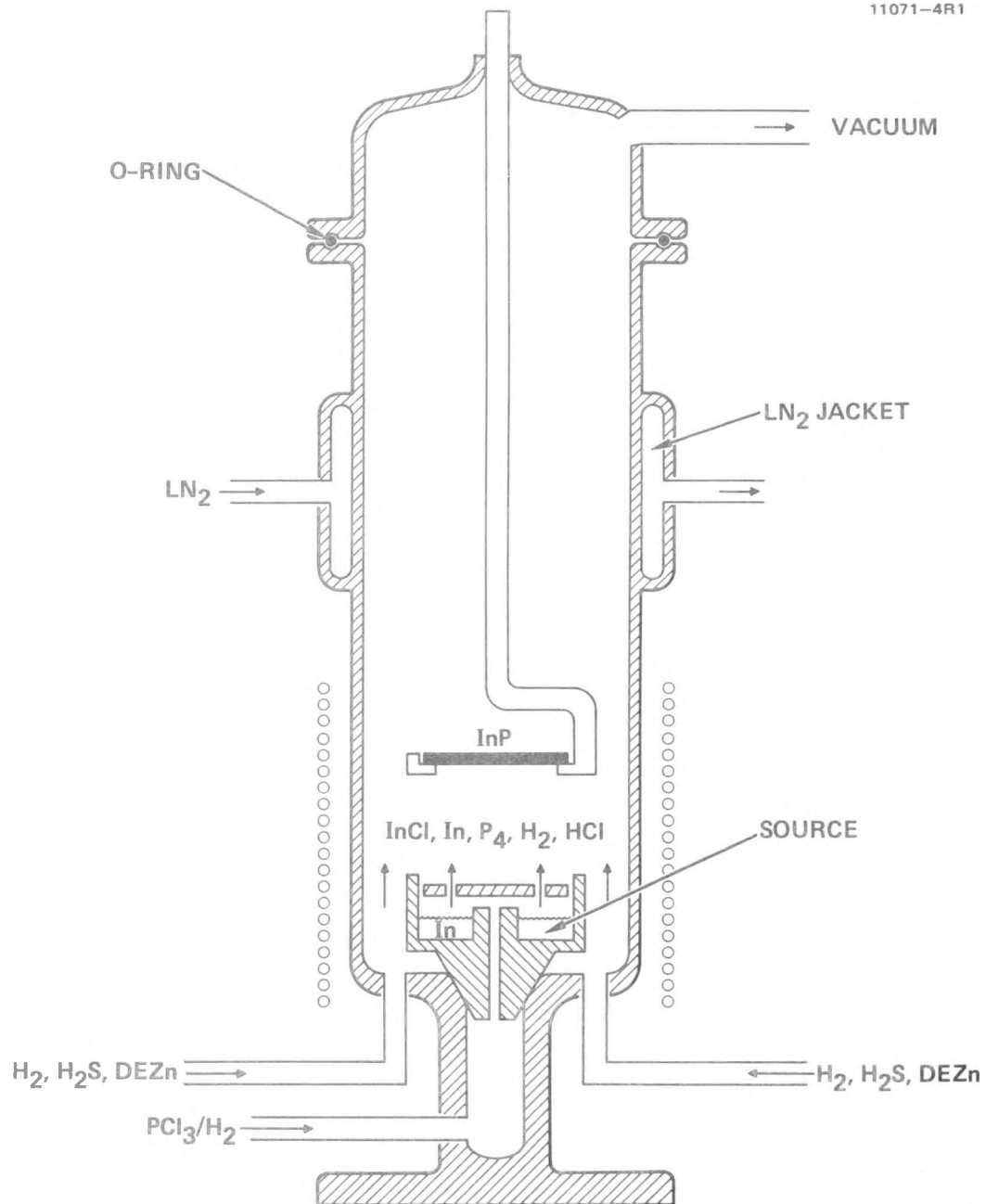


Figure 25. Low pressure InP/PCl₃ reactor.

SECTION 4

SUMMARY AND RECOMMENDATIONS

Whether the thin-film InP/CdS solar cell is practical or not depends primarily upon the availability of In. This issue has not been resolved. From a technical point of view, progress in developing the all thin-film cell has been hindered by the difficulty in simultaneously obtaining p-type InP and grains of InP with large lateral dimensions.

We have grown thin-films of InP on RxCdS and have found that above substrate temperatures of 320°C p-type material can be prepared, but that the dimensions of the grains are only on the order of microns. An analysis of the interfaces indicates that at 380°C an InCdS transition region a few tenths of a micron thick exists. The transition region is less than $100 \text{ \AA}$ thick at substrate temperatures below 320°C . It is not positively known whether this transition layer interferes with the preparation of good epitaxial InP. Due to the uncertainty in controlling diffusion down grain boundaries, it was decided to concentrate studies at a lower temperature of 280°C where InP grains with large lateral dimension can be achieved. Unfortunately, material grown at this temperature is n-type even though SIMS analysis of the material shows the material to contain the p-type dopant Be. Therefore, we shifted our efforts toward studying the behavior of Be-doped InP on semi-insulating InP substrates at 280°C . At this temperature the material is also n-type, even though SIMS shows the presence of Be at levels which make the material p-type if prepared at a higher temperature.

At approximately 330°C , MBE data² shows a transition from a reconstructed surface at a higher temperature to an atomically smooth surface at a lower temperature. Undoped InP was deposited on (100) semi-insulating InP, and the electron concentration was examined as a function of the ratio of the phosphorus to indium fluxes. The purpose of the experiment was twofold. First, it was intended to alter the nature of the surface (i.e., reconstructed versus atomically smooth). A change in surface kinetics might alter the electrical properties. Second, it was intended to change the native defect and impurity

incorporation in the bulk, regardless of the surface kinetics. These studies were done with unintentionally doped films on (100) semi-insulating substrates at 330°C. The electrical properties did not depend upon the flux ratio, indicating either an impurity controlled conductivity and/or a conductivity controlled by non-equilibrium concentration of native defects.

Several approaches should be considered to obtain an all thin-film InP/RXCdS solar cell. First, attempts should be made to reduce the transition temperature above which p-type films can be made. Growth in a halogen environment and the formation of the volatile specie InCl at the surface should alter In surface kinetics and might lower the transition temperature at which a reconstructed to an atomically smooth surface occurs.

The second alternative is to grow a thin, 0.1 μm thick, n-type InP epitaxial film to provide a buffer layer which permits the subsequent epitaxial growth of p-type InP at a higher temperature. This approach eliminates the materials constraint of preparing a single InP film on RXCdS, which must simultaneously contain large grains and be p-type.

The third alternative is to prepare a frontwall cell containing a tunnel junction. In this structure, an n^+ InP epitaxial layer is prepared at 280°C, as in Figure 26. This buffer layer will permit the growth of an epitaxial p^+ layer at a higher temperature of 350°C. A p-type layer would be deposited on the p^+/n^+ tunnel junction at the same temperature. Light would be incident on an ITO or CdS transparent top contact.

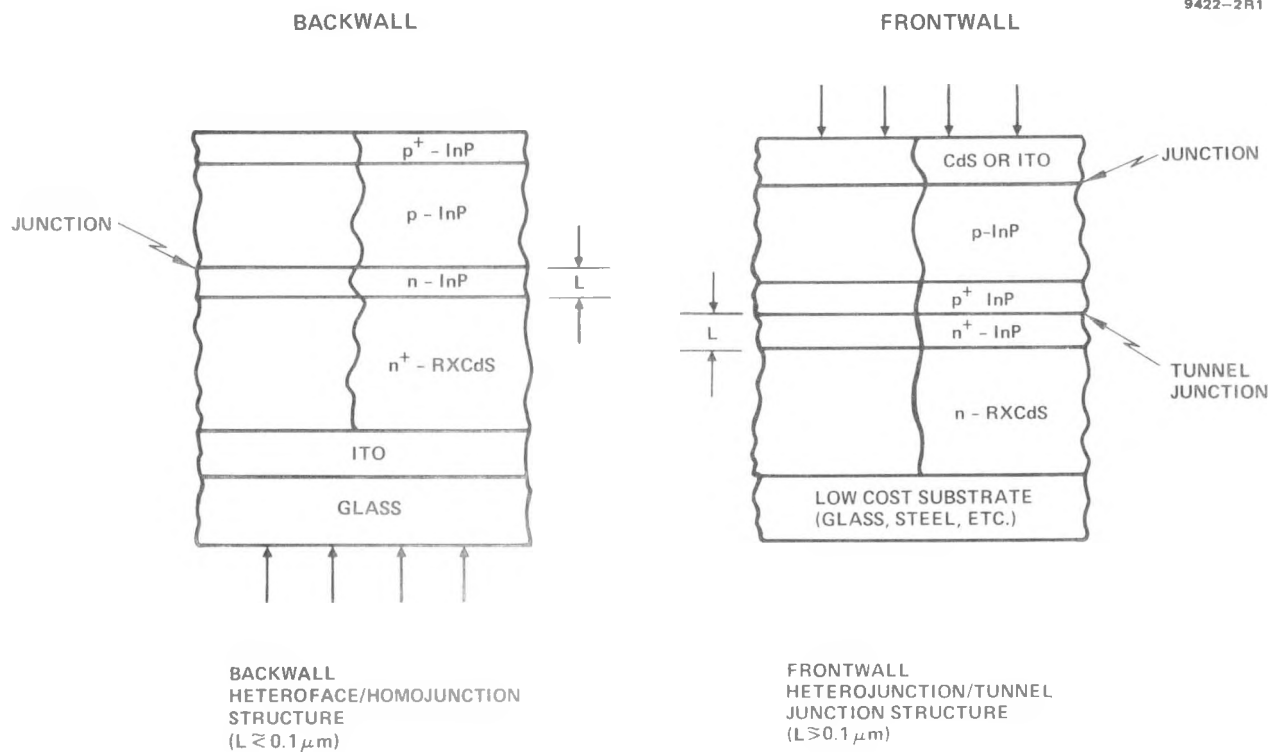


Figure 26. All-thin-film InP/CdS solar cells utilizing the backwall (left) and frontwall (right) structures.

SECTION 5

REFERENCES

1. S. Wagner, J.L. Shay, K.J. Bachmann, E. Buehler, and M. Bettini, J. Crystal Growth 39, 128 (1977).
2. M.T. Norris, Appl. Phys. Lett. 36, 282 (1980).
3. J.H. McFee, B.I. Miller, and K.J. Bachmann, J. Electrochem. Soc. 124, 259(1977).
4. J.P. Duchemin, M. Bonnet, G. Beuchet, and F. Koelsch, "Gallium Arsenide and Related Compounds," Inst. Phys. Conf. St. Louis, Mo., 1978, Ser. 45, p. 10.
5. "InP by Planar Reactive Deposition and GaAs by Low Pressure Metal Organic Chemical Vapor Deposition," Final Report to F44620-76-C-0133.
6. L. Fraas and K. Zanio, J. of Electronic Materials 7, 211(1978).
7. "SIMS Analyses of InP Films," by Handord Engineering and Development Laboratory, Richland, Washington (1980).
8. N.G. D'here and N.R. Parikh, J. Vac. Sci. Technol. 17, 714(1980).
9. A.R. Calawa, Appl. Phys. Lett. 38, 701(1981).

APPENDIX A

Large Grains of InP and CdTe on Recrystallized CdS Substrates

Large grains of InP and CdTe on recrystallized CdS substrates

Frans Krajenbrink, Peter Hoberg, Hank Montano, and Ken Zanio
Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, California 90265

(Received 30 June 1980; accepted for publication 20 November 1980)

Thin films ($\sim 1\ \mu\text{m}$) of large-grained ($\sim 40\ \mu\text{m} \times \sim 40\ \mu\text{m}$) InP were epitaxially deposited on low-cost recrystallized CdS substrates at 280°C by planar reactive deposition. Large grains of CdTe ($\sim 40\ \mu\text{m}$) were also deposited on similar substrates at 460°C by physical vapor deposition. Typically, the recrystallized CdS grain size is about $40\ \mu\text{m}$. However, grains with dimensions up to $300\ \mu\text{m}$ were observed.

PACS numbers: 81.10.Bk

InP,¹ GaAs,² and CdTe (Ref. 3) are promising semiconductors for all thin-film solar cell systems. Unfortunately, the development of these systems, especially those using III-V compounds, is inhibited by the unavailability of a low-cost substrate. We have suggested the use of recrystallized CdS on indium tin oxide on glass (RXCdS/ITO/Glass) as a low-cost substrate.⁴ In this paper we report a substantial increase in the grain size and further development of the RXCdS substrate. More importantly, we report for the first time the epitaxial deposition of large area but thin films of a III-V compound on a low-cost substrate. We also describe the preparation of large grains of CdTe on the same substrate by low-temperature physical vapor deposition.

As described in earlier publications,^{4,5} about $20\ \mu\text{m}$ of CdS is thermally deposited on ITO/Glass. The CdS is then recrystallized. Figure 1 shows optical (left) and x-ray Read (right) pictures of three different CdS films at different stages of processing. The thermally deposited films consist of submicrometer size grains. The orientation of the grains are such that the *c* axis is preferably aligned normal to the substrate. The preferred orientation results in arcs rather than continuous rings on the x-ray Read picture.

As the recrystallization process proceeds in flowing H_2S at 500°C (as previously described),⁵ the grain size increases and the grains adopt a more random orientation. The Read picture of the incompletely recrystallized film (middle) contains both arcs characteristic of submicrometer grains of preferred orientation and random discrete spots characteristic of large grains of randomly oriented CdS. Clusters of discrete spots also indicate a small fraction of the large grains to have a preferred orientation. In these Read pictures, the discrete spots due to the $\text{Cu}_{K\alpha}$ and $\text{Cu}_{K\beta}$ radiation are superimposed on a background of discrete spots due to white radiation. Only discrete spots are found in the picture (bottom) for the fully recrystallized film. It is generally, but not always, true that the recrystallization as indicated by the x-ray film is more complete with increasing grain size. However, an exception is demonstrated here. The Read picture for the film having the larger grains (middle) shows arcs, which are characteristic of submicrometer size grains having a preferred orientation. The average grain size of our films has increased from $30\ \mu\text{m}$ in earlier work to $50\ \mu\text{m}$. Grains with lateral dimensions up to $0.3\ \text{mm}$ have been observed. No quantitative reason for the increase in grain size is known. As expected, we also found that the yield of recrystallized films improves as the cleanliness of the deposition system

and the ITO/Glass substrates improves. The yield of obtaining an average grain size of at least $30\ \mu\text{m}$ is about 80%.

After films are recrystallized, the sheet resistance is in excess of $10^5\ \Omega/\square$. However, by firing RXCdS in a Cd overpressure at 500°C , the sheet resistivity is reduced to a typical value of about $20\ \Omega/\square$. Values as low as $10\ \Omega/\square$ have been obtained. Absorption losses are about 10% over wavelengths ranging from 0.5 to $1.0\ \mu\text{m}$.

InP was deposited on RXCdS by planar reactive deposition⁴ (PRD) at substrate temperatures of 280 – 380°C at a rate of about $2\ \mu\text{m}/\text{hr}$. No special preparation was given to the RXCdS film. After firing in Cd overpressures, they were stored in air. Before the InP deposition, they were thermally etched in PH_3 for 30 min at a temperature 50°C above the deposition temperature. At a substrate temperature of 380°C , there is about a $0.5\text{-}\mu\text{m}$ -thick In-Cd-S transition layer between the InP and CdS. X-ray Read pictures of these InP/RXCdS films show rings composed of fine spots. For these films, scanning electron microscope (SEM) pictures show a "wormy" looking surface. The characteristic dimension of these films is several times larger than the characteristic dimension of polycrystalline films deposited on ITO/Glass. A casual examination of x-ray Read pictures of the wormy looking surfaces shows continuous rings. However, a more careful examination shows the rings to be composed of discrete spots, which indicates that the degree of epitaxy is superior to that indicated by the SEM. However, the dimensions of the InP grains are much smaller than those of the RXCdS. At the 380°C substrate temperature, the In-Cd-S transition layer between the InP and CdS presumably degrades the quality of the epitaxy. Unintentionally doped films are always *n* type. Films doped with Be are *p* type when the RXCdS is capped (i.e., when the diameter of the InP deposition is larger than diameter of the RXCdS substrate). When the RXCdS is not capped, the films are always *n* type, presumably due to sulfur doping via vapor transport.

Complete epitaxy was obtained at 280°C on the RXCdS grains, which have dimensions of about $40\ \mu\text{m}$. Figure 2 (top) shows SEM pictures of InP epitaxy on a single RXCdS grain. Only at higher magnifications can the facets of the grains be resolved. It is evident that the facets are aligned over the entire photograph. The middle picture shows InP epitaxy covering two adjacent grains of RXCdS. There is a distinct difference in the orientation of the facets across the grain boundary. In the bottom picture, this grain boundary

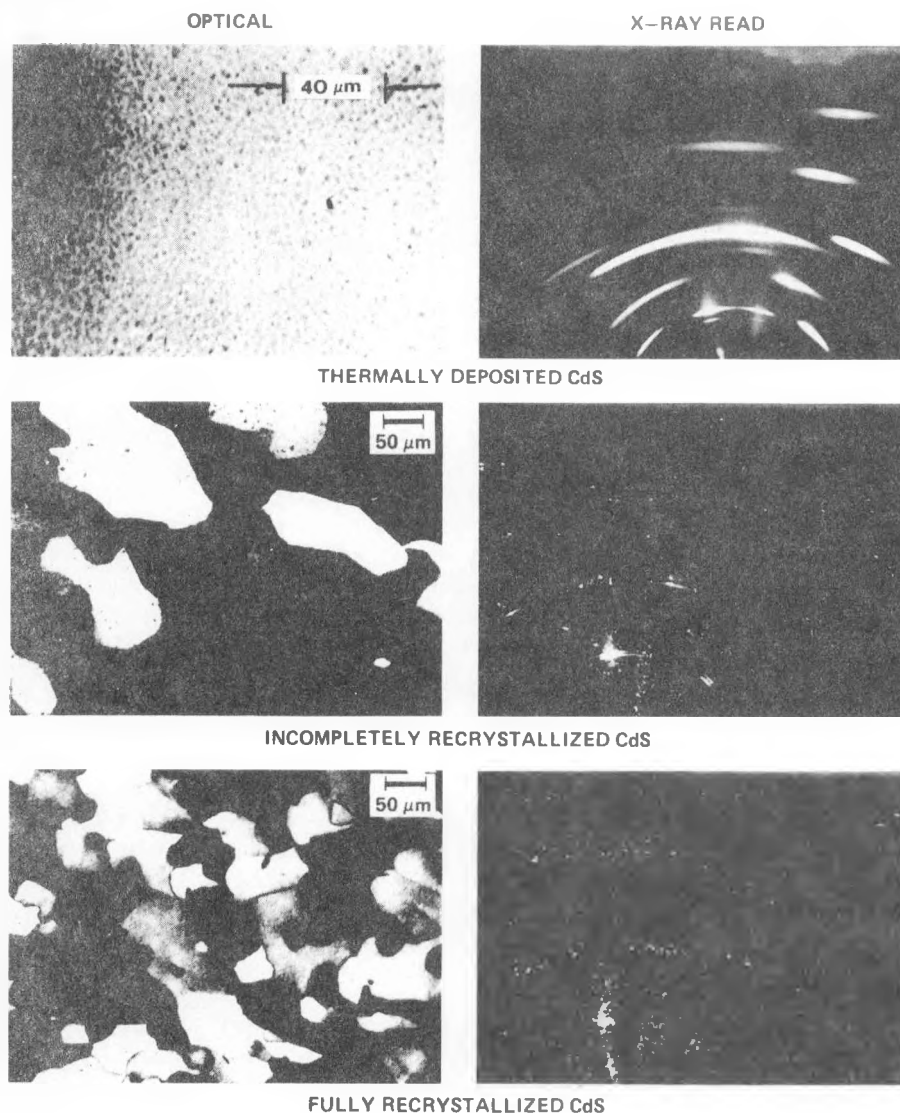


FIG. 1. Optical (left) and x-ray Read (right) pictures of (top) a thermally deposited and unrecrystallized CdS film, (middle) an incompletely recrystallized CdS film, and (bottom) a fully recrystallized CdS film. Photographs of the thermally deposited films were taken in unpolarized light, whereas photographs of the recrystallized films were taken in transmitted polarized light.

is delineated to better contrast the orientation of the two grains. The x-ray Read picture (Fig. 3, top) shows the characteristic discrete spots also seen for the RXCdS film. There is some indication that the InP film contains submicrometer grains with preferred orientation. However, these submicrometer grains are believed to replicate regions of the CdS that are not completely recrystallized. Complete epitaxy of InP on RXCdS is not typically obtained. We are presently investigating the growth conditions in more detail to improve the reproducibility. It is likely that, for a substrate temperature of 280 °C, a thin In-Cd-S transition layer also exists in our InP/RXCdS structure. Dhere and Parikh⁶ occasionally found two new hexagonal structures and also a cubic superstructure when they vacuum deposited InP films of a few hundred angstroms on CdS/NaCl at 300 °C. However, it appears from our results that thin transition layers will not seriously degrade the replication of InP grains on RXCdS grains. Unintentionally doped films prepared at 280 °C on

(100) InP substrates are *n* type. Be-doped films prepared at 280 °C are also *n* type, presumably due to a rapid increase in the *n* type native defect concentration below a substrate temperature of 320 °C.

CdTe was also deposited on RXCdS at 460 °C in a physical vapor deposition (PVD) system. This system is a modification of an earlier system⁷ for growing CdTe by PVD. Growth was undertaken in a 2-in.-diam. flat-bottomed vertical quartz ampoule with the RXCdS substrate located at the bottom of the ampoule. A CdTe source at ~600 °C was located 1 in. above the substrate. Samples were loaded through a 2-in.-diam. stainless-steel flange located at the top of the ampoule. The ampoule containing the source and the substrate were first outgassed at 100 °C and 10^{-7} Torr. Then the source and substrate were brought up to the growth temperature, and CdTe was deposited at a rate of ~30 μm/hr.

Figure 4 shows SEM pictures of ~30-μm-thick CdTe films deposited on (top) RXCdS and (bottom) ITO/Glass

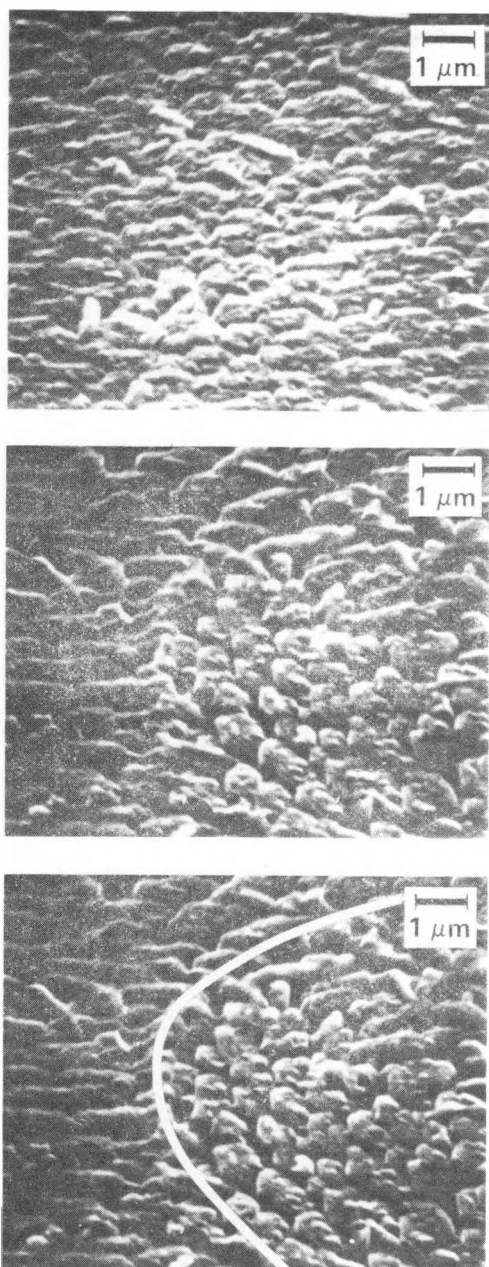


FIG. 2. InP deposited by PRD at 280 °C on (top) a single RXCdS grain, (middle) two RXCdS grains, and (bottom) the same two RXCdS grains but with the grain boundary delineated.

substrates. For the CdTe grown on the RXCdS, the average grain size is about 40 μm . For CdTe grown on the ITO/Glass substrate, the grain size is about an order of magnitude less. A more direct comparison in the middle figure at a low magnification shows CdTe grown both on and off the RXCdS. The x-ray Read picture (Fig. 3, bottom) confirms the presence of the large CdTe grains. Thin films of CdTe with grains as large as 70 μm have recently been prepared by CVD at 620 °C on unrecrystallized CdS.⁸ However, the lower growth temperatures possible with physical vapor deposition are preferred in preparing CdTe thin-film solar cells, as vacuum processing is more likely to result in smooth, continuous films and to be a more economical technology.

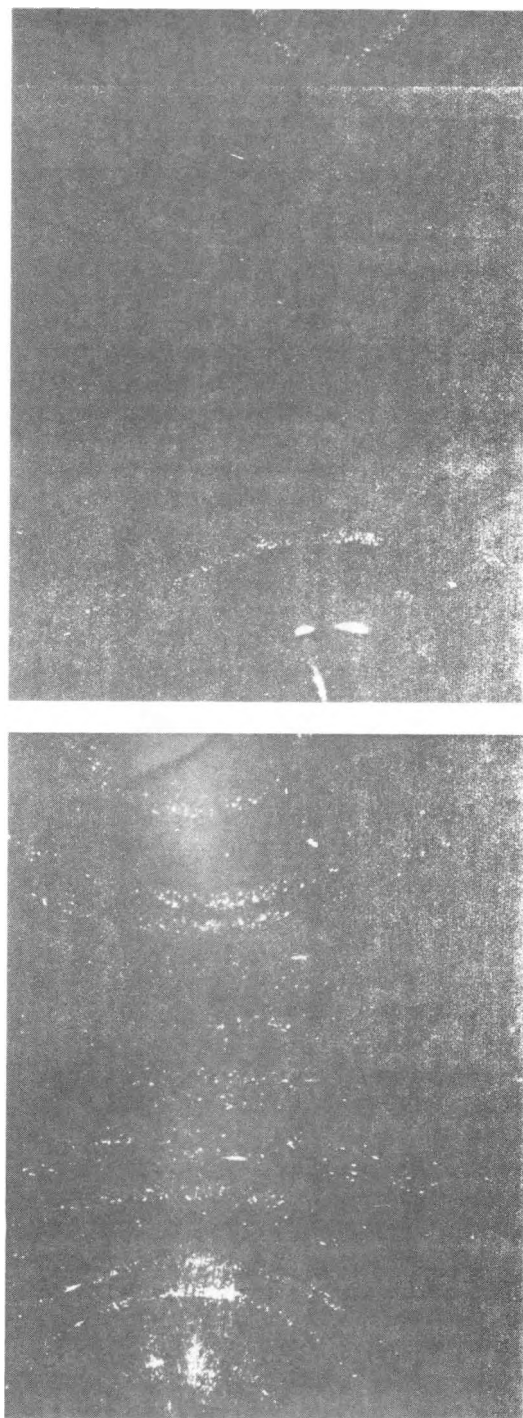


FIG. 3. X-ray Read pictures of InP (top) and CdTe (bottom) deposited on RXCdS.

The morphologies of the CdTe and InP layers are quite different. Compared to InP, the CdTe grains have larger facets. Enhanced facet size is due in part to the higher substrate temperature for the CdTe, as a higher substrate temperature enhances surface mobility. However, even under similar growth conditions, the CdTe facets should be larger than the InP facets due to differences between the binding

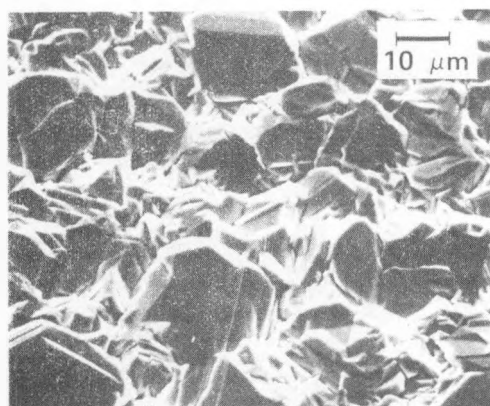
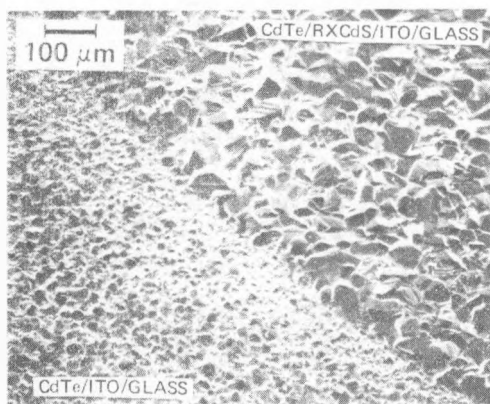
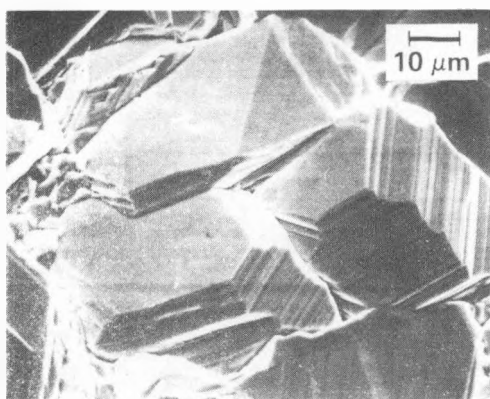


FIG. 4. SEM pictures of CdTe deposited on (top) RXCdS and (bottom) ITO/GLASS. The middle picture directly compares the grain size of CdTe deposited on RXCdS to that on ITO/GLASS.

energies of crystal planes. Unlike the InP, it is not evident that the CdTe replicates the RXCdS. In the CdTe growth, the larger grains appear to crowd out the smaller ones.

The preparation of large grains of InP on a low-cost substrate lends support to further development of the InP/CdS system. These results rule out the possibility that an In-Cd-S transition layer would prevent the epitaxial deposition of large grains of polycrystalline InP on CdS. Potential problems do exist, however. A high concentration of *n*-type native defects at lower substrate temperatures may interfere with intentional *p*-type doping. The extent of sulfur diffusion and consequently *n*-type doping in the *p*-type InP will determine whether the development of this device will be directed towards a backwall or frontwall device.

An increase in the grain size of the CdTe for solar cells is not as important as for the III-V compounds because the leakage currents at the grain boundary in the wide band gap II-VI materials are not as severe. Difference in device performance between the single-crystal and polycrystalline CdTe/CdS systems are not expected to be as extreme as in the InP/CdS systems because the lattice mismatch between the CdTe and CdS will affect device performance regardless of grain size.

The authors thank Ken Miller and Art Timper for the x-ray Read pictures, Jerry Meldrum for the SEM pictures, and Roger Turk for the optical photographs. This work was administered by SERI on DOE Contract XJ-9-8170-1.

- ¹S. Wagner, J. L. Shay, K. J. Bachmann, E. Buehler, and M. Bettini, *J. Cryst. Growth* **39**, 128 (1977).
- ²W. Johnston and W. Callahan, *J. Electrochem. Soc.* **125**, 977 (1978).
- ³N. Nakayama, H. Matsumoto, A. Nakano, S. Ikegami, H. Uda, and T. Yamashita, *Jpn. J. Appl. Phys.* **19**, 703 (1980).
- ⁴L. M. Fraas and K. Zanio, *J. Electron. Mater.* **7**, 211 (1978).
- ⁵L. M. Fraas, W. P. Bleha, and P. Braatz, *J. Appl. Phys.* **46**, 491 (1975).
- ⁶N. G. Dhere and N. R. Parikh, *J. Vac. Sci. Technol.* **17**, 714 (1980).
- ⁷W. Akutagawa and K. Zanio, *J. Cryst. Growth* **11**, 191 (1971).
- ⁸M. Bettini and G. Brandt, *J. Appl. Phys.* **50**, 869 (1979).

Permission to reprint this
copyrighted article granted by
American Institute of Physics and
Hughes Research Laboratories.

☆U.S. GOVERNMENT PRINTING OFFICE: 1981-740-145/2965