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SERI/PR-9196-1-T2

INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

Semiannual Report for the Period July–December 1980

By
K. Zanio

MASTER

March 1981

Work Performed Under Contract No. AC02-77CH00178

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Hughes Research Laboratories
Malibu, California



U.S. Department of Energy



Solar Energy

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INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

K. Zanio

**Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, CA 90265**

March 1981

Contract XZ-0-9196-1

**Semiannual Report
July 1980 through December 1980**

**Prepared for
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Washington, DC 20545**

**Monitored by
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Golden, CO 80401**

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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 is being 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 is Dr. Zanio. Principal investigators are Dr. Zanio and Mr. F. Krajewski. Important contributions to the program were made by Messrs. K. Miller, P. Hoberg, H. Montano, and A. Timper. SIMS analyses were provided by Hanford Engineering Development Laboratory (HEDL) under separate contract to SERI. Valuable discussions with Dr. David Greenslade of HEDL are acknowledged. Additional SIM and Auger services were purchased from Charles Evans and Associates through this contract.

Abstract

InP thin films were deposited by planar reactive deposition on recrystallized CdS (RXCdS) and semi-insulating (100) InP substrates and evaluated as potential layers for an all-thin-film solar cell. Films prepared on RXCdS at approximately 330°C contained a mixture of grains having both large and submicron lateral dimensions. SIMS analysis showed the interdiffusion profiles to be well behaved and, within the resolution of the analysis, no significant difference in the profiles between structures prepared at 330°C and 380°C.

Be-doped epitaxial films, deposited on semi-insulating InP at 330°C, showed both n- and p-type behavior. Films prepared at higher and lower temperatures with a freshly Be-charged In source were p-type and n-type, respectively; the n-type behavior is associated with an excess of n-type native defects. SIMS analyses confirmed the presence of Be in all Be-doped films. Growth with deviation from stoichiometry was initiated at 330°C to reduce the concentration of native defects.

Growth of Be-doped films at higher substrate temperature with the same Be-doped source after several runs eventually resulted in n-type films. Analyses of the In source and films were initiated to determine the cause of the transient doping. As an alternative to Be doping, p-type Zn-doped InP films were prepared on InP semi-insulating substrates with room-temperature carrier concentrations and mobilities of 6×10^{16} cm⁻³, and 80 cm²/Vsec, respectively.

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SECTION 1
INTRODUCTION

This report summarizes the efforts at Hughes Research Laboratories (HRL) for the first two quarters on this contract to develop the InP/CdS system for an all-thin-film solar cell. The approach (Figure 1) is to prepare a thin film of p-type InP on recrystallized CdS (RXCdS). By growing epitaxial InP on the RXCdS, we could achieve a large lateral grain size with only a micron-thick layer of InP. By the end of DOE contract XJ-9-8170-1 we had prepared large grains ($\approx 40 \mu\text{m}$) of RXCdS on glass. We had also deposited epitaxial n-type InP thin films with a large lateral grain size ($\approx 40 \mu\text{m}$) on RXCdS at 280°C . Be-doped films were not p-type. We also prepared p-type films on RXCdS at 380°C , but the lateral dimensions of the InP were of submicron dimensions. The next step to develop the InP/CdS system as an all-thin-film solar cell is to prepare InP on RXCdS that is simultaneously p-type and has grains with large lateral dimensions.

During this period we prepared InP on RXCdS at the intermediate substrate temperature of 330°C with the intention of simultaneously achieving large grains and p-type material. These results are discussed in Section 2. In Section 3 we describe further studies to understand and enhance the electrical activity of Be in InP at low substrate temperatures. Studies related to transient p-type doping by the source are also discussed here. In Section 4 we propose alternate multilayer InP/CdS structures consisting of large grained n-type InP layers deposited on the RXCdS at low temperature, and large grained p-type InP layers deposited on the n-type InP at a higher temperature

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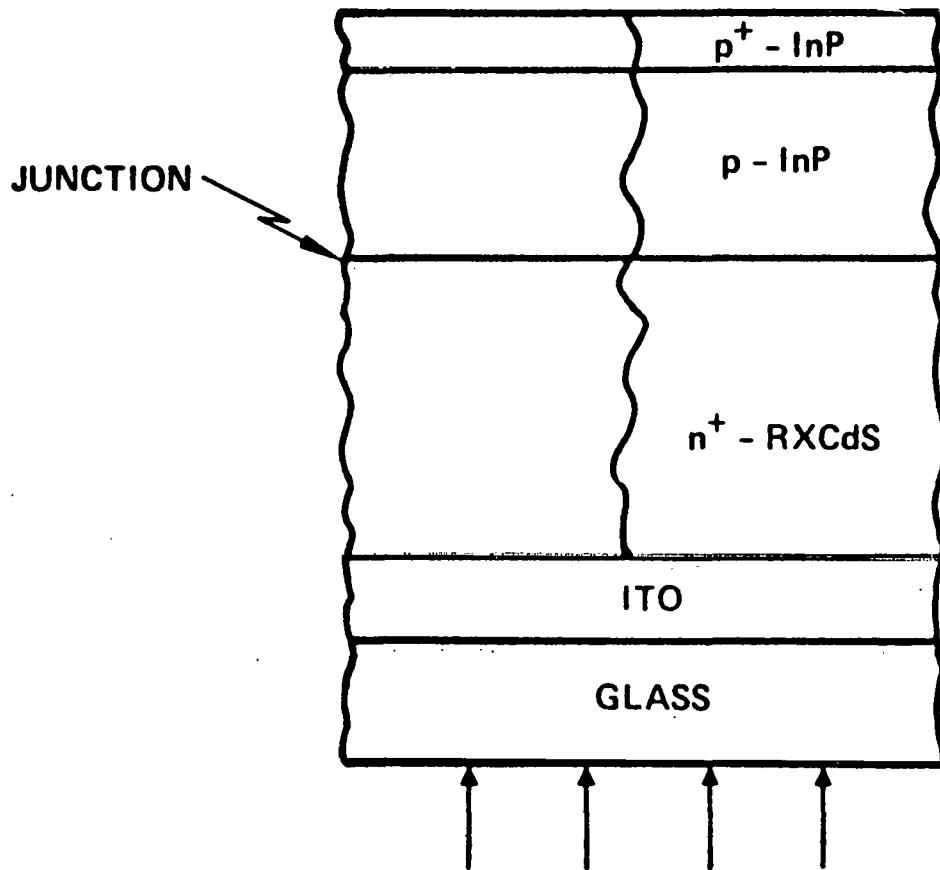


Figure 1. All-thin film InP/CdS solar cell utilizing the concept of the growth of a thin, but large grained InP film on recrystallized CdS.

SECTION 2

InP EPITAXY ON RXCdS

During this period we prepared several films of InP on RXCdS at 330°C. Figure 2 shows scanning electron microscope (SEM) and corresponding x-ray Read pictures of InP films prepared on RXCdS at 280°C, 330°C, and 380°C. The results at 280°C, obtained in the previous program, 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. At the other extreme, the SEM of the film prepared at 380°C shows 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 are of intermediate quality. The SEM shows faceting, but the facets are not oriented, and the grain boundaries are not evident. These films are of unacceptable quality. 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, or severe deviations from stoichoimetric CdS.

We are continuing studies to determine the composition of the transition region. We know that for InP prepared on CdS at about 425°C there is an In-Cd-S transition region about 1 μm thick between the InP and the CdS. At 380°C the transition region is on the order of 0.3 μm . The measurements at 425°C were made by scanning cleaved structures with a microprobe. The results at 380°C were obtained by optical examination and composition measurements of films (a few tenths of a micron thick) deposited on RXCdS. InCdSP layers deficient in P have a wide

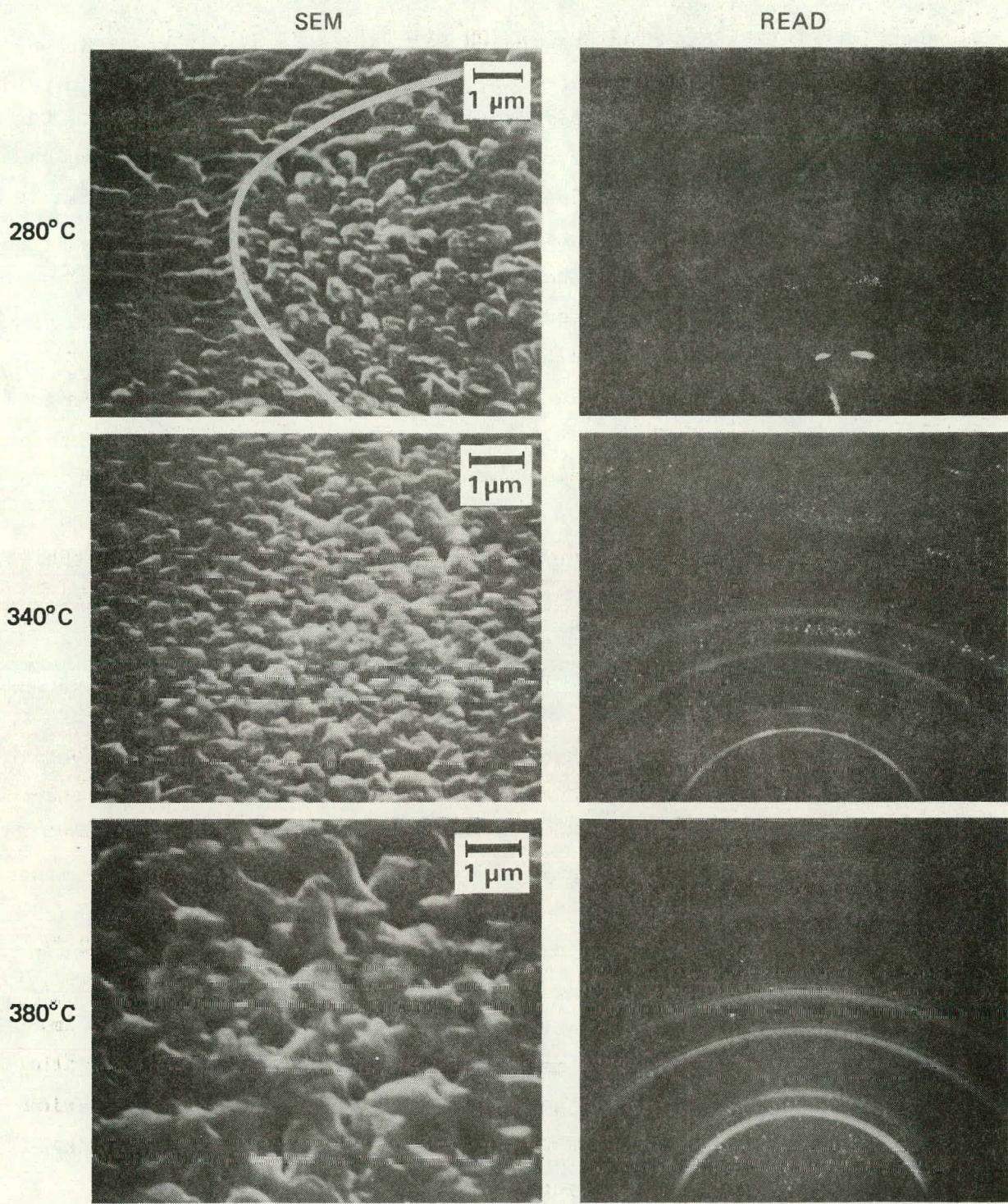


Figure 2. SEM and x-ray Read pictures of InP deposited on RXCdS at different substrate temperatures.

bandgap and are as transparent as the CdS. Hanford Engineering Development Laboratory (HEDL) has also undertaken SIMS profiles of InP/RXCdS structures. Figure 3 shows SIMS profiles for In, Cd, P, S, Be, and Al of a 4- μm -thick Be-doped film deposited on RXCdS at 380°C. An oxygen beam was used to detect 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. (Multiply the abscissa by the factors in the legend to find counts per second for each specie.) The interface is clearly defined. Microprofilometry by HEDL shows this film to be about 4.5 μm thick.

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 support the thesis that the increased ^{115}In and reduced $^{147}\text{InO}_2$ count rates were ionization artifacts. The HEDL analyses will be included in its entirety in our final report. The P profile suggests P depletion at the interface. This would be consistent with earlier results which indicated P depletion at the interface. However, we feel this also to be an artifact of the ionization process for two reasons. First, the STMS 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. Second, the degree of depletion does not decrease with a decrease in the substrate temperature.

Figure 4 show profiles for In, Cd, P, and Al for an undoped n-type 2- μm -thick InP film desposited 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 3 and 4, respectively. Although a Be/Al alloy was not incorporated in the source, SIMS analysis evidenced Al, and also found Al to be distributed locally at the InP/CdS interface. We obtained good epitaxial growth of

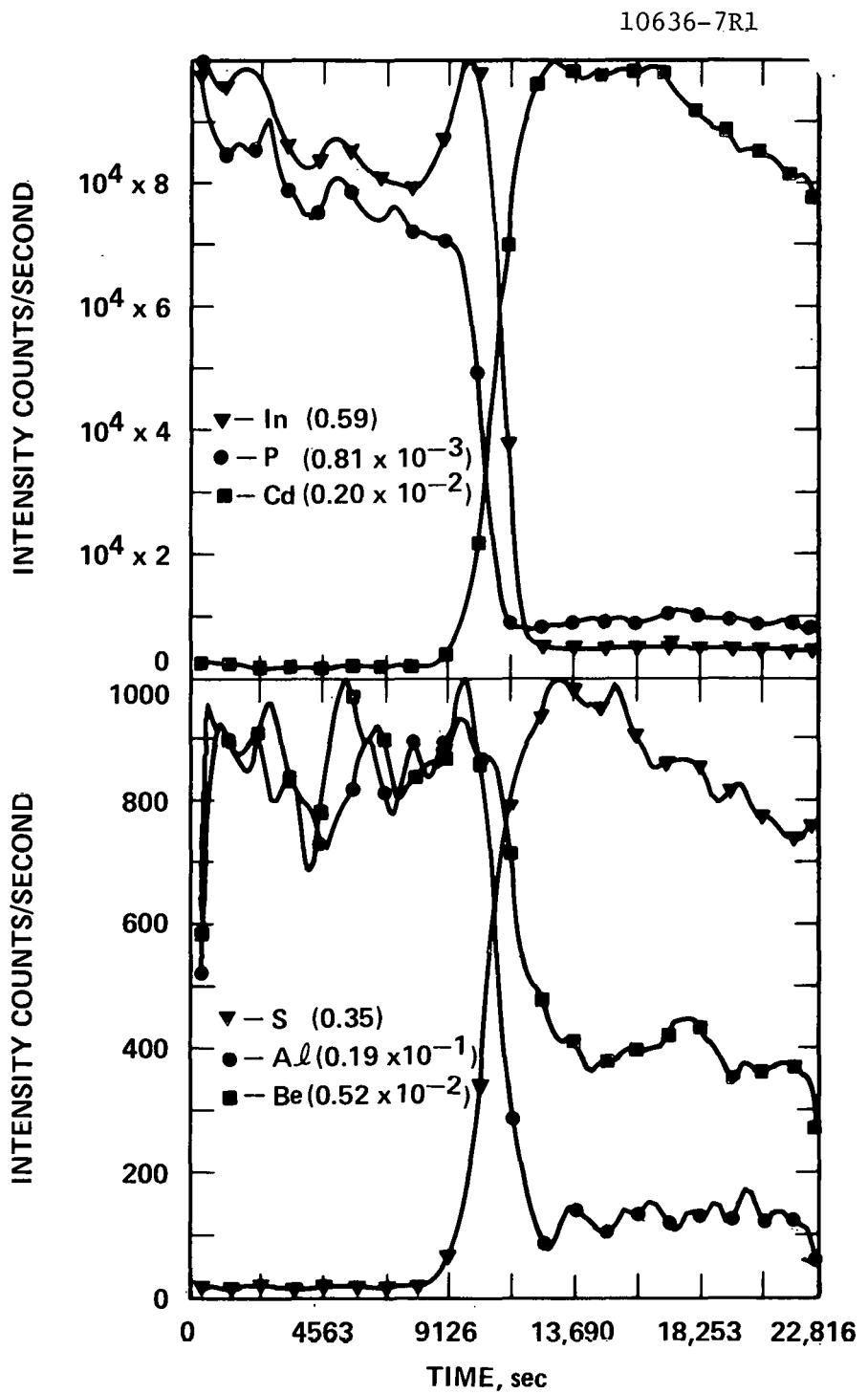


Figure 3. SIMS profiles p-InP/RxCdS for InP deposited at 380°C.

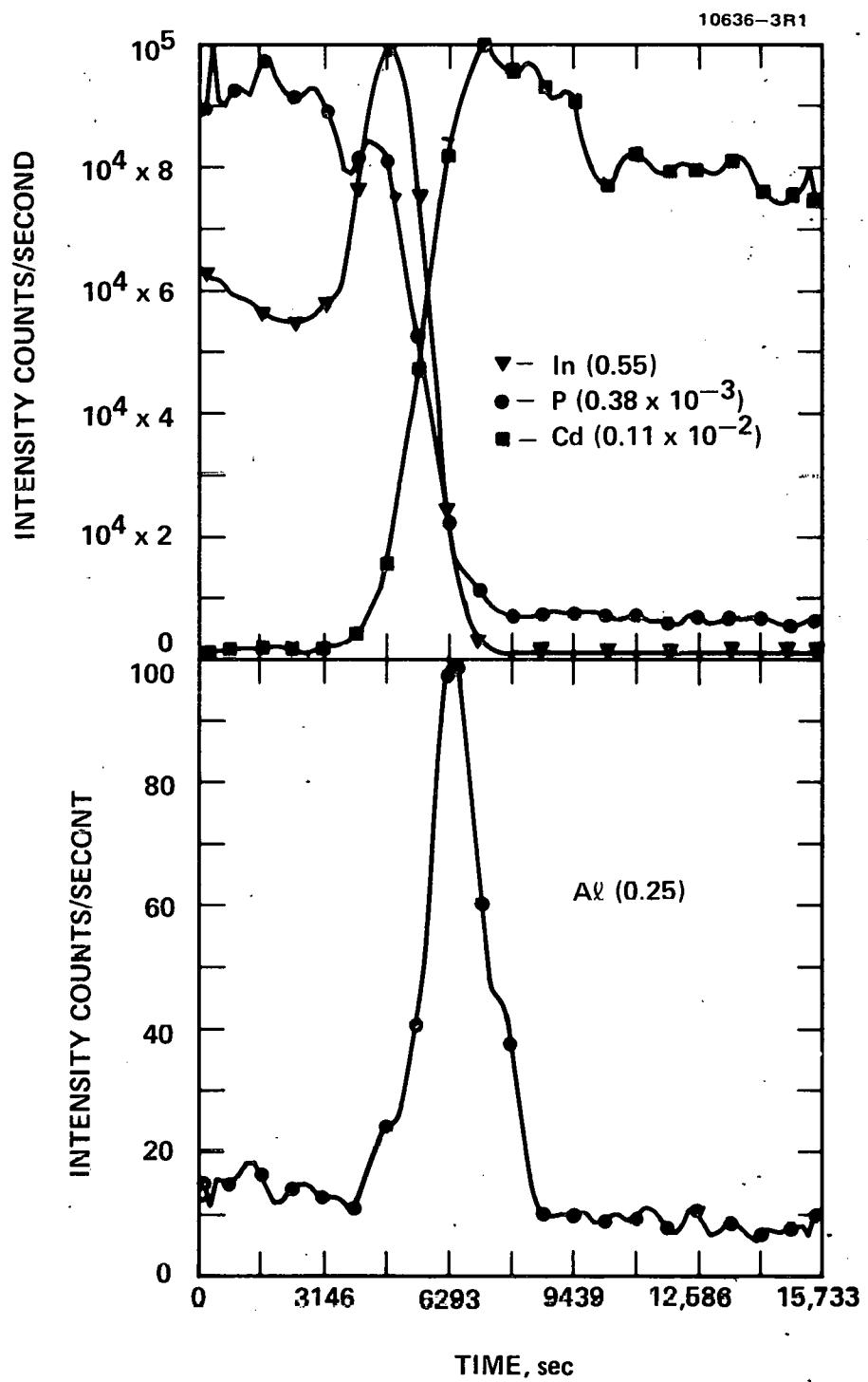


Figure 4. SIMS profiles n-InP/RxCdS for InP prepared at 330°C.

InP on RXCdS at lower substrate temperatures using intentional Be/Al doping. Further studies are necessary to verify that Al was incorporated. If so, further efforts will be necessary to determine the source of Al.

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 confirm that severe interdiffusion between InP and CdS does not occur. From our microprobe and optical studies, and the SIMS data of HEDL, we estimate the interdiffusion distances for InP deposited on RXCdS at 280°C to be on the order of 300 Å. This thickness is probably overestimated as transmission electron microscope measurements of 100 Å thick films of InP prepared on CdS at 300°C show no transition region.¹

Additional studies are necessary to solve the extraneous nucleation problem. Slower sputtering rates at the interface are necessary to determine the composition at the interface. Films of InP on the order of 100 Å must be grown on RXCdS. These films must then be examined with SEM and SIMS to track the nucleation and growth process.

SECTION 3

P-DOPING OF InP FILMS

If p-type films could be grown at reduced substrate temperatures it would not be necessary to eliminate extraneous nucleation on substrates at higher temperatures. To assist in determining the electrical properties of InP on RXCdS, and to assist in understanding why p-type films cannot be prepared at low substrate temperatures, we deposited InP on semi-insulating substrates.

Figure 5 shows the general behavior of the type, and carrier concentration for InP on seminsulating InP substrates for several runs subsequent to charging In sources to similar levels of Be. 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 about 330°C, both n- and p-type films are obtained. However, only n-type films are eventually obtained with the same source. At a substrate temperature of 300°C or less, only n-type films are initially obtained. There are two problems. The first is associated with the substrate. The electrical properties appear to depend on the substrate temperature. The second problem is associated with the source. For example, at a substrate temperature of 380°C using the same Be-doped source, the type changes from p to n type in successive runs. Most likely, the flux of Be atoms decreases with the number of depositions. The substrate problem is discussed in the following; the source problem is discussed in Section 3-B.

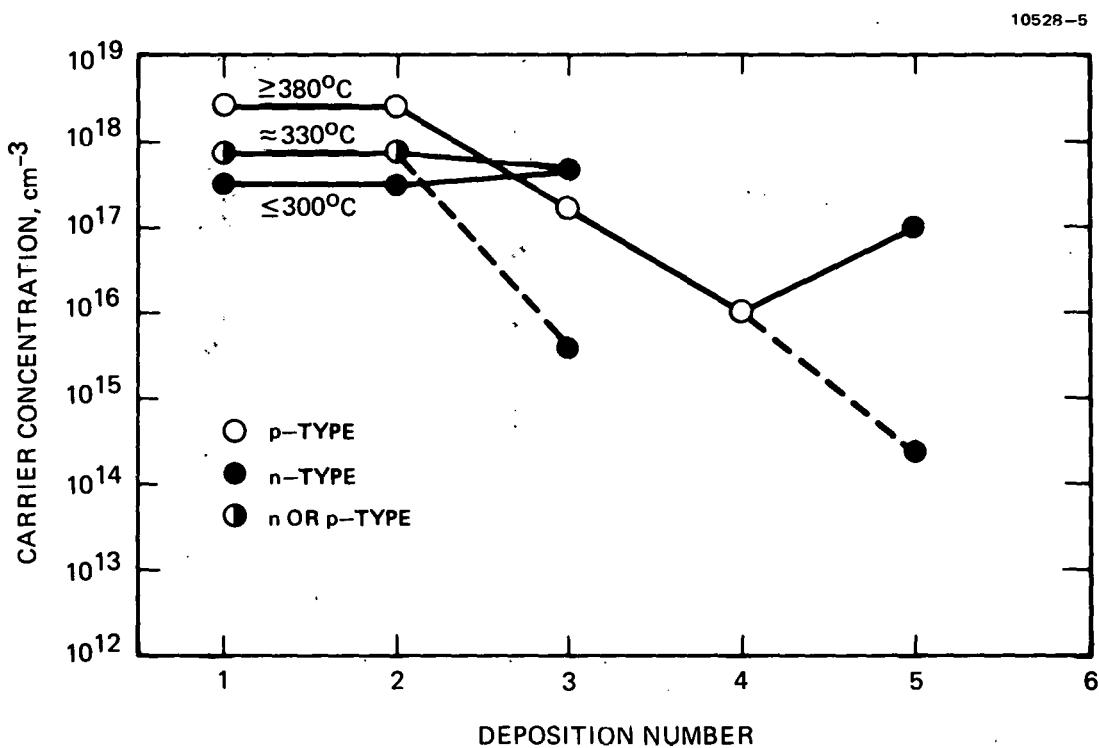


Figure 5. Type and carrier concentration of InP films prepared at various substrate temperatures, versus the number of depositions after charging the In source with similar levels of 5%/95% by weight Be/Al alloy.

A. ELECTRICAL ACTIVITY OF Be IN InP

To verify that Be was present in our films for runs undertaken with freshly charged Be sources, HEDL performed SIMS analyses on these films. Figure 6 shows SIMS profiles for In, P, Be, Al, and Ga for p-type InP prepared on semi-insulating InP at a substrate temperature of 380°C. Gallium is present in our system because it is used to make contact between the source heater plate and Cu electrodes. The concentration of Ga and Al in our films as estimated from microprobe analysis is less than 1%. They are isoelectronic impurities, and if incorporated uniformly in the InP at this level without oxides, are not expected to affect the electrical, optical, and crystallographic properties of our films. An abrupt decrease in the Be, Al, and Ga profiles occur at the interface. The profile of Al falls off more rapidly than the profile of Be, possibly because Al finds a stable location on the InP cation sublattice, and does not readily diffuse into the CdS. Beryllium probably exists interstitially, and is a rapid diffuser in both InP and CdS.

Figure 7 is a SIMS profile for P, Be, Al, and Ga in Be-doped InP prepared at an InP substrate temperature of 300°C. Note that the interfaces for Be, Al, and Ga are even more abrupt and similar. The slopes at the interfaces are probably limited by the resolution of the SIMS at this sputtering rate. These SIMS data have verified that Be is present in our n-type InP films.

The absence of p-type conductivity is probably a result of the presence of n-type native defects. Figure 8 shows the carrier concentration and mobility of unintentionally doped films of InP prepared by vacuum technologies on InP substrates. All films are n-type. The carrier concentration and the mobility, respectively, increase and decrease with decreasing substrate temperature, at a substrate temperature of about 300°C for all of the work reported. Since the same general behavior has been observed at different laboratories, it is

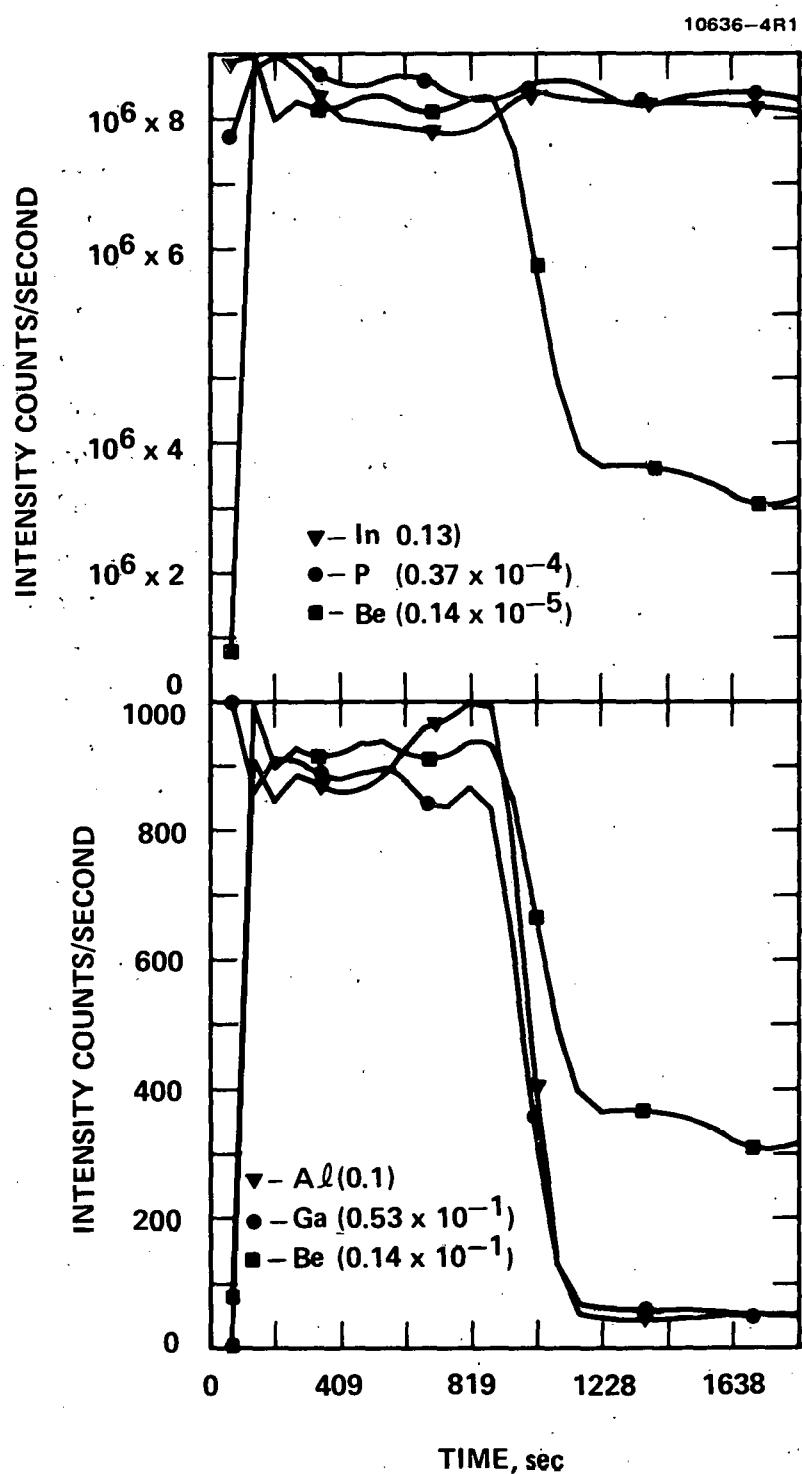


Figure 6. SIMS profiles p-InP/InP for InP prepared at 380°C.

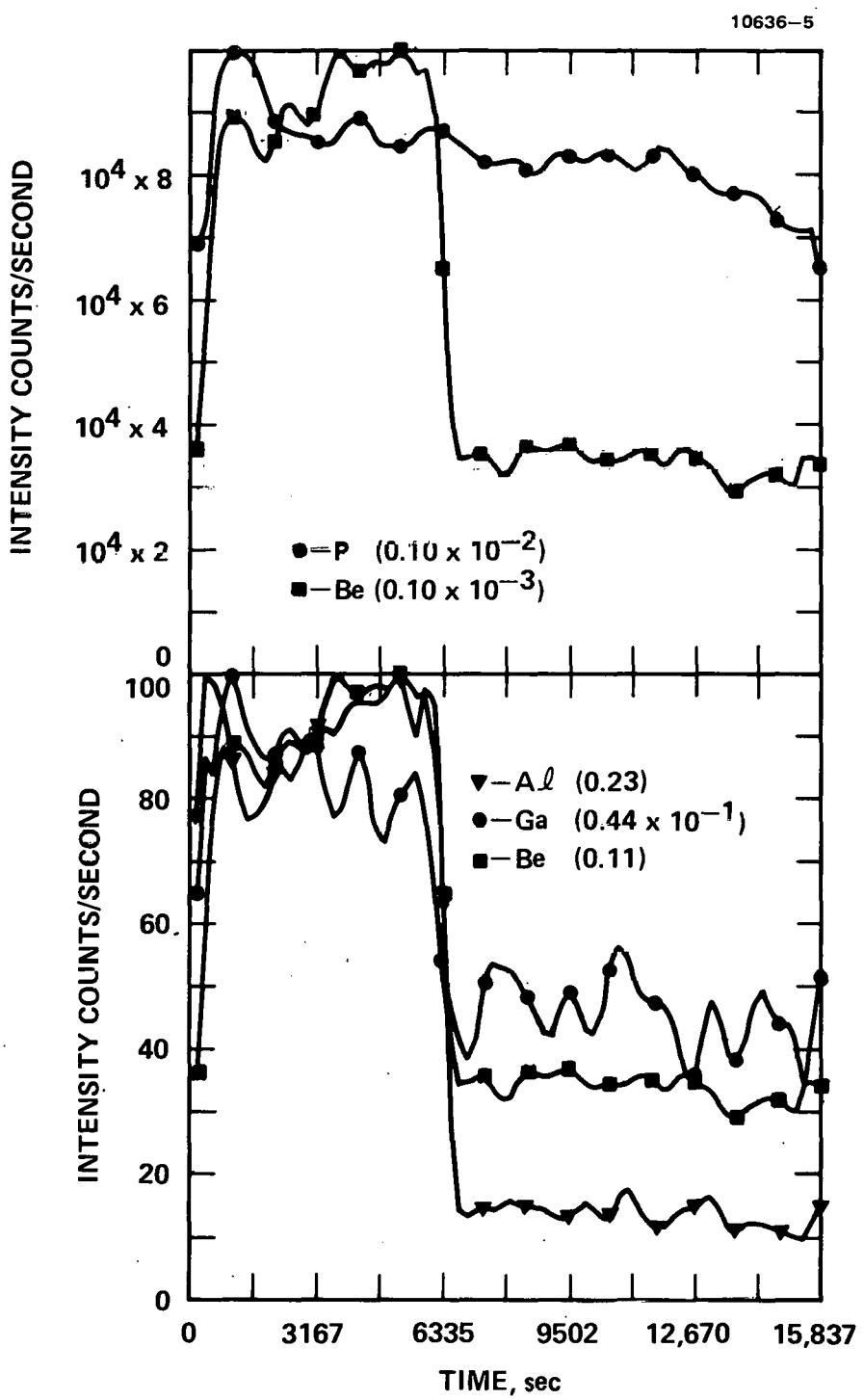


Figure 7. SIMS profiles n-InP/InP for InP prepared at 300°C.

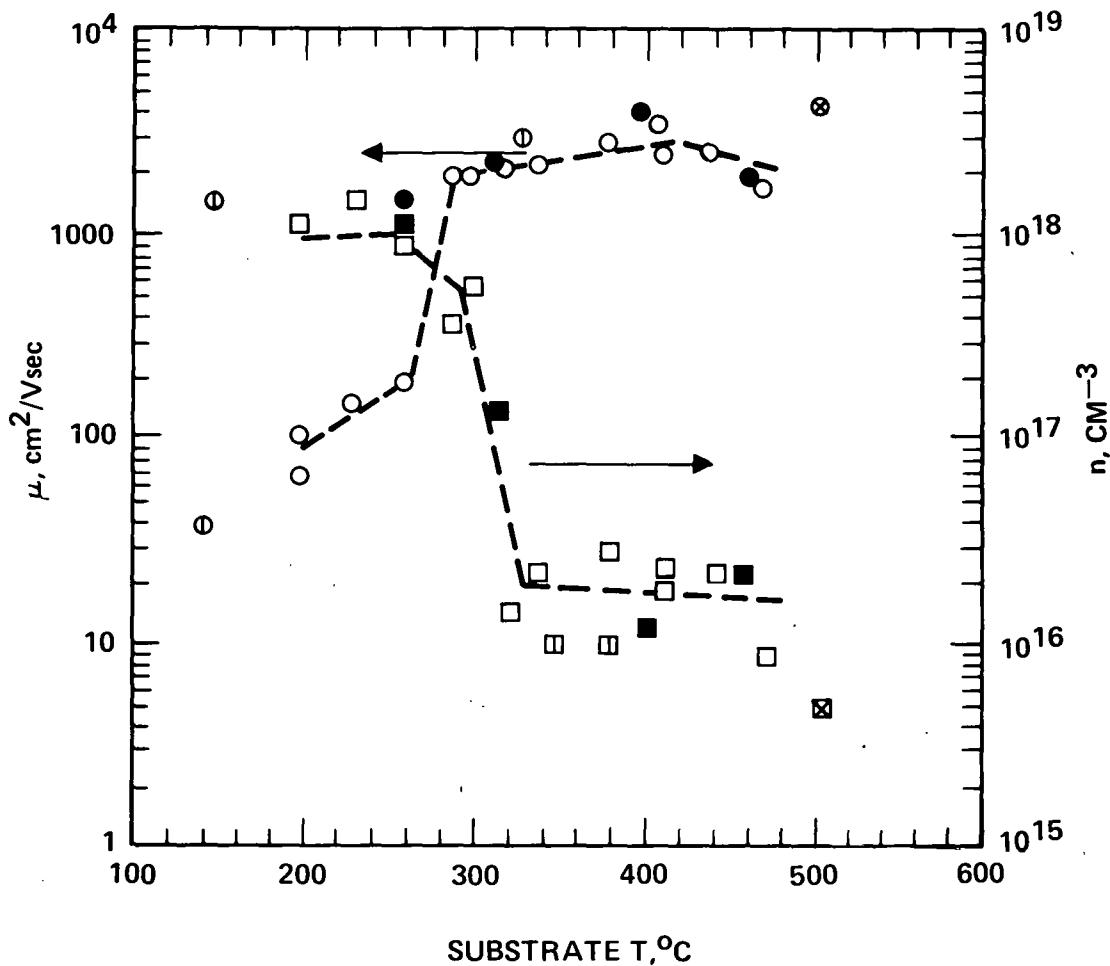


Figure 8. Unintentionally doped InP films prepared on InP substrates by vacuum technologies.

likely a native defect rather an impurity effect. It is necessary to reduce the concentration of native defects below 10^{17} cm^{-3} before we can make p-type films for solar cells.

One method to reduce the concentration of native defects is to change the deviation from stoichiometry. Such effects have been observed in GaAs prepared by molecular-beam epitaxy (MBE) and metal-organic chemical-vapor deposition (MOCVD)⁵. We include some of our MOCVD work on a completed AFOSR program (F44620-76-C-0133) to illustrate this. Figure 9 shows the carrier concentration versus the AsH_3 to $(\text{CH}_3)_3\text{Ga}$ flow rate ratio ($F_{\text{AsH}_3}/F_{\text{TMGa}}$) for GaAs prepared by MOCVD. Films are p-type at low $F_{\text{AsH}_3}/F_{\text{TMGa}}$. The films become less p-type with increasing $F_{\text{AsH}_3}/F_{\text{TMGa}}$. With further increases in $F_{\text{AsH}_3}/F_{\text{TMGa}}$, the carrier concentration reaches a minimum. The films become n type with increasing carrier concentration. At the minimum carrier concentration, the total concentration of the electrically active impurities, $N_A + N_D$, is near its minimum value. Changes in the carrier concentration should also occur in the InP system. It is therefore important to find where the minimum concentration of electrically active native defects occur. In the GaAs system a $N_A + N_D$ below 10^{16} cm^{-3} can be routinely achieved. Achieving a $N_A + N_D$ of 10^{17} cm^{-3} would be adequate in our InP films. We have begun deviation from stoichiometry studies for InP grown by PRD. Figure 10 shows the electron concentration versus the ratio of the PH_3 partial pressure to the In growth rate, $P_{\text{PH}_3}/F_{\text{In}}$. Data at low $P_{\text{PH}_3}/F_{\text{In}}$ correspond to growth near the three-phase boundary. Our material is n-type near the In-rich side of the three-phase boundary. Our carrier concentration appears to decrease with increasing $P_{\text{PH}_3}/F_{\text{In}}$. However, additional data must be taken to confirm these results. We hope the carrier concentration at high $P_{\text{PH}_3}/F_{\text{In}}$ will be well below 10^{17} cm^{-3} . We must operate at higher $P_{\text{PH}_3}/F_{\text{In}}$ ratios to determine if the carrier concentration reaches

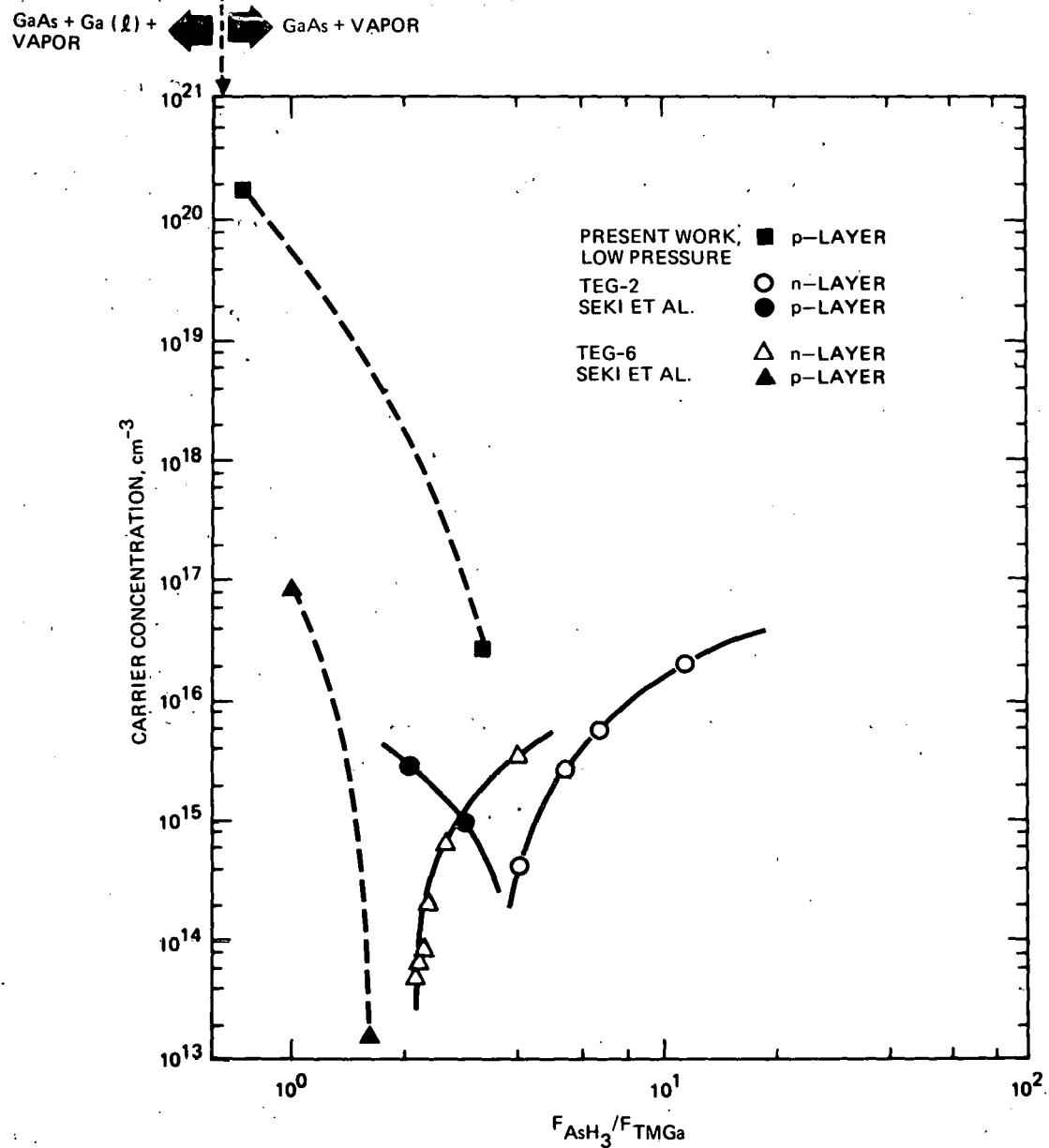


Figure 9. The dependence of type and carrier concentration on the ratio of the AsH_3 to TMGa fluxes for GaAs prepared by MOCVD. (The low-pressure work was sponsored by AFOSR under Contract F44620-76-C-0133.)

10^{17} cm^{-3} . Our data were taken with a phosphine source which contained a 10% PH_3 /90% H_2 mixture. In the next quarter we will change to a higher PH_3/H_2 mixture to test this hypothesis.

The important difference between the GaAs and InP systems is that for growth near the cation-rich three-phase boundary, GaAs is p-type whereas InP is n-type. This difference might be related to the type of bonding in GaAs and InP. GaAs bonding is highly covalent and the tetrahedral covalent radii are equivalent. The Group IV atoms substitute easily for Ga and As resulting in n- and p-type doping, respectively. In fact, Ga could substitute for As, resulting in further p-type doping as suggested by studies in our AFOSR program. However, InP is more ionic and the tetrahedral covalent are significantly different. Because InP is more ionic it follows a more conventional defect structure; i.e., excess In resulting phosphorus vacancies and n-type behavior. Therefore it is not energetically favorable in the InP system for either Group IV impurities or the cation (In) to occupy anion (P) sites to result in p-type doping.

B. TRANSIENT p-TYPE DOPING WITH Be

1. The Source Problem

Figure 5 shows that in successive runs at 380°C with a freshly charged Be-doped source, the degree of p-type doping decreases. Either the source does not deliver a constant flux of Be atoms, or it delivers a constant flux of Be. Nevertheless, the Be is rendered electrically inactive by an impurity such as oxygen. Oxidation of the Be in the source is one possible reason for the transient effect. As the system is opened up after each run, Be is oxidized at the surface. Eventually, most of the Be is gettered by the oxygen. Exposure of the source to oxygen is easy to avoid in a production environment, but not so easy to avoid during these research studies. It is therefore necessary to know the concentration and distribution of Be atoms in the source and in the films as a function of the number of runs after charging the source.

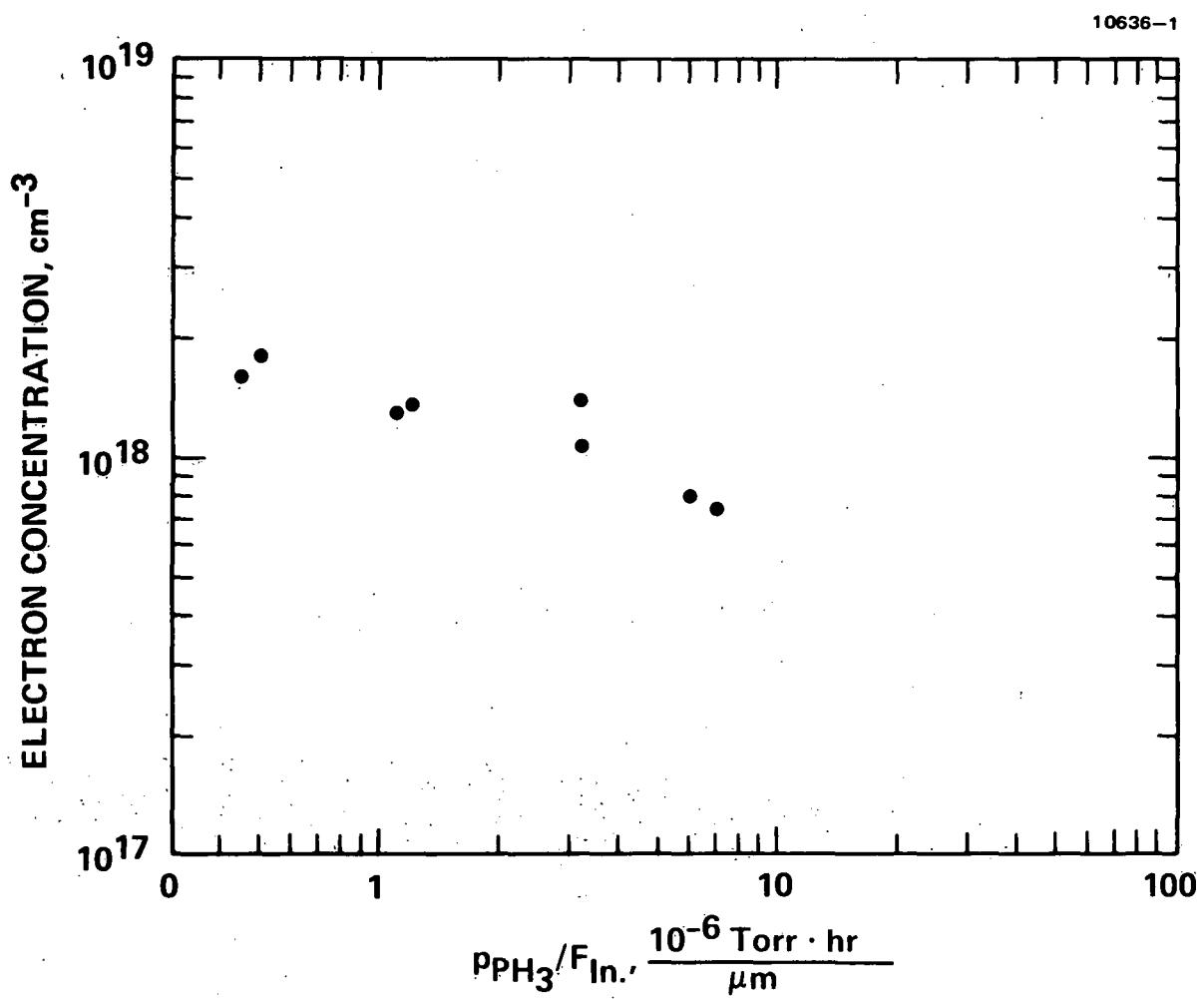


Figure 10. Electron concentration of undoped InP prepared at 330°C PRD versus the ratio of the reactants.

The films analyzed for Be and described previously were prepared in the first few runs after changing the source. We are planning to analyze additional films which have been prepared with an old source. In the meantime, we have begun a microprobe analysis of our film. We undertook an analysis of several Be-doped films with our microprobe, but it was not sensitive enough to detect Be. However, Al was detected in some of our films at about 1% (see Figure 11). When our film, indicated by the dots, is compared with the InP reference substrate, an Al peak becomes apparent to the left of the phosphorus peak. Al is present on our films because Be is incorporated in the In source as a 5%/95% by weight Be/Al alloy. At high levels of Al, and presumably also of Be, the quality of the epitaxy degrades. Figure 12 shows SEM and corresponding selective area electron diffraction (SAD) pictures of a layer containing \approx 1% Al. This figure also contains SEM and SAD pictures of a layer having less than 1% 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, because the film contain less than 1% Al.

Although our microprobe is not sensitive enough to detect Be, these studies imply high concentrations of Be through the presence of Al. In addition, they suggest that achieving high concentrations of Be would degrade the quality of the epitaxy due to the required higher concentrations of Al. The latter is not understood since Al is a column III element and should substitute for In in low concentration without degrading the quality of the epitaxy. The quality would be degraded if a large concentration of oxygen were included along with the Al and Be. HEDL has begun an analysis of C and O in the films described in Section 3. When those results are received we will extend them to films prepared with an "old" source.

We also sent an undoped In source to Charles Evans & Associates for SIMS and Auger analysis. Figure 13 shows their results acquired by

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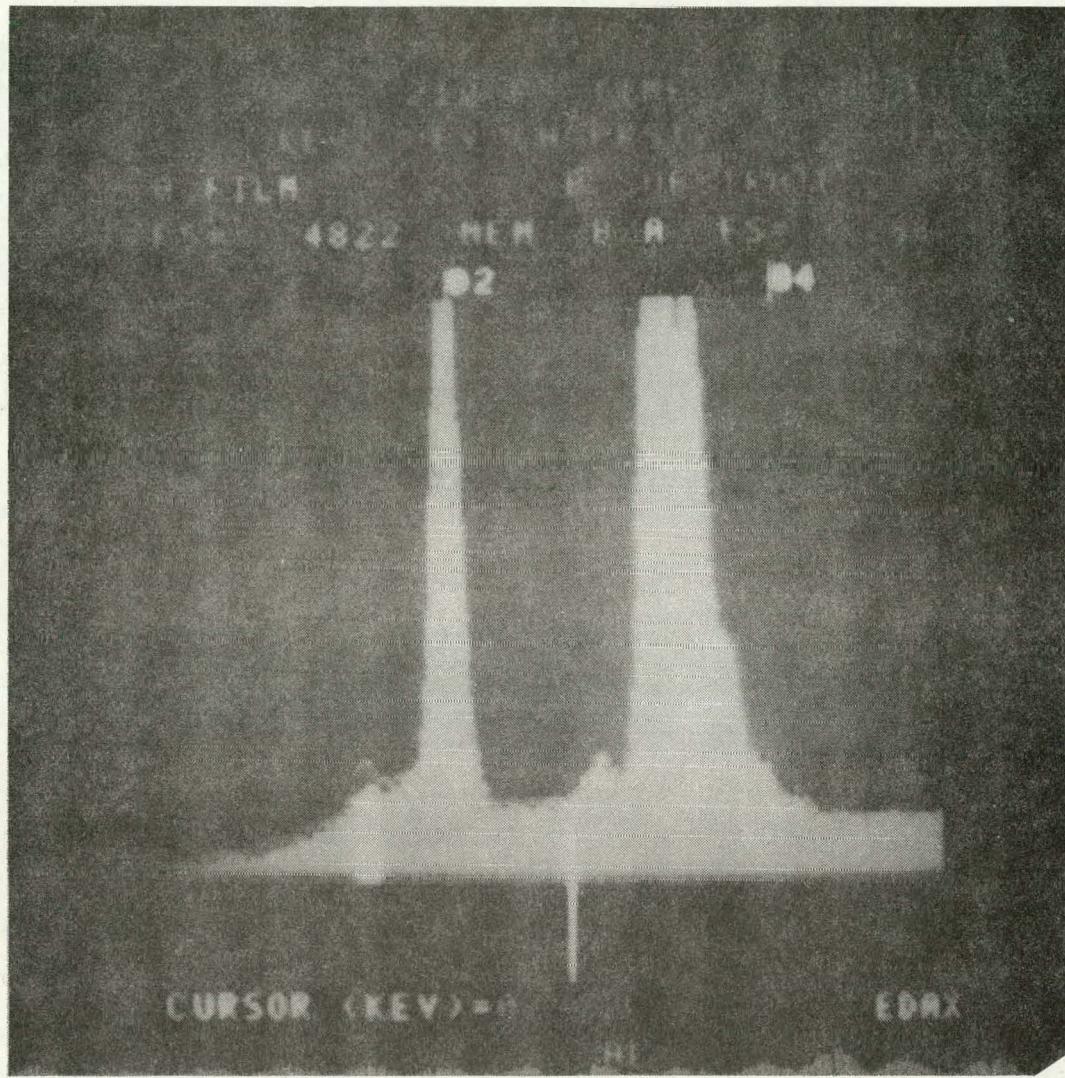
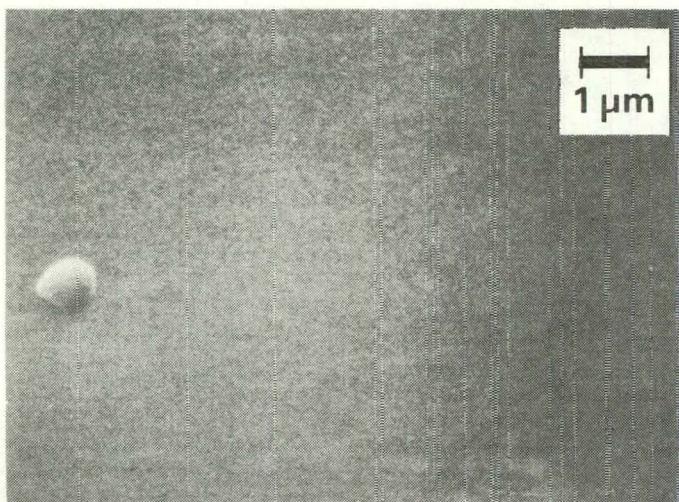


Figure 11. Microprobe analysis of Be-doped InP film showing about 1% Al.

SEM



SAD

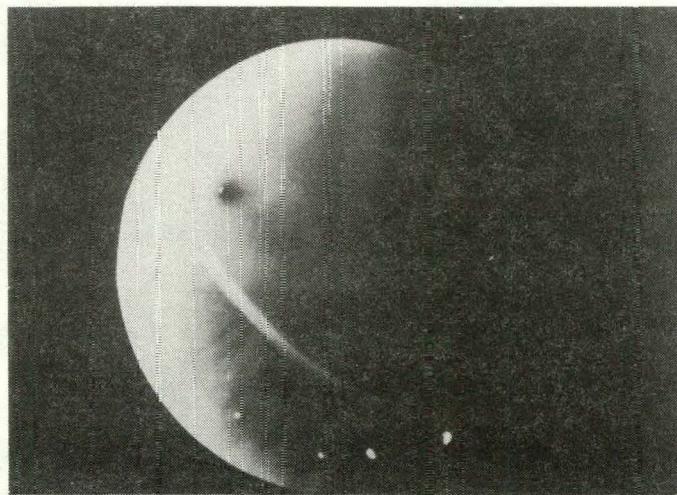
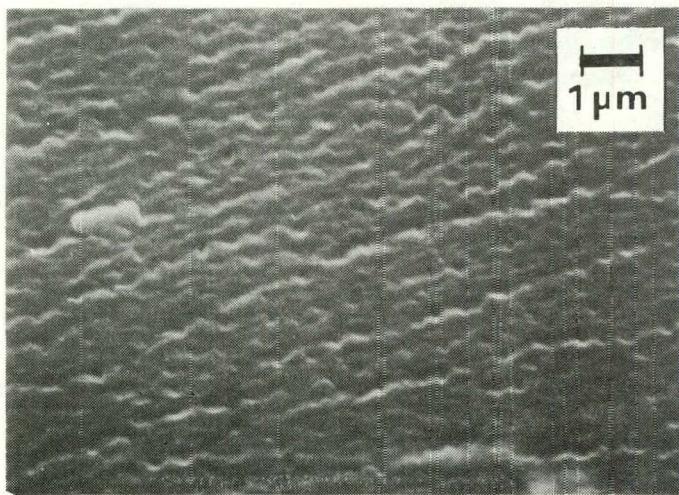
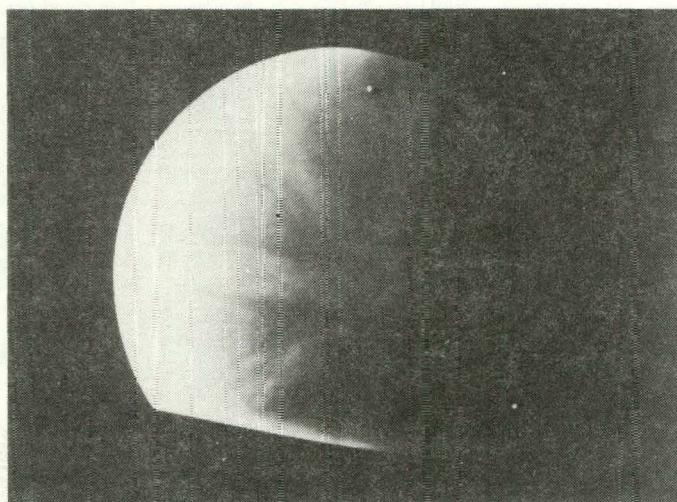


Figure 12. SEM and corresponding SAD pictures of Be/Al-doped InP films prepared at 330°C containing (top) less than 1% and (bottom) approximately 1% of Al by microprobe analysis.

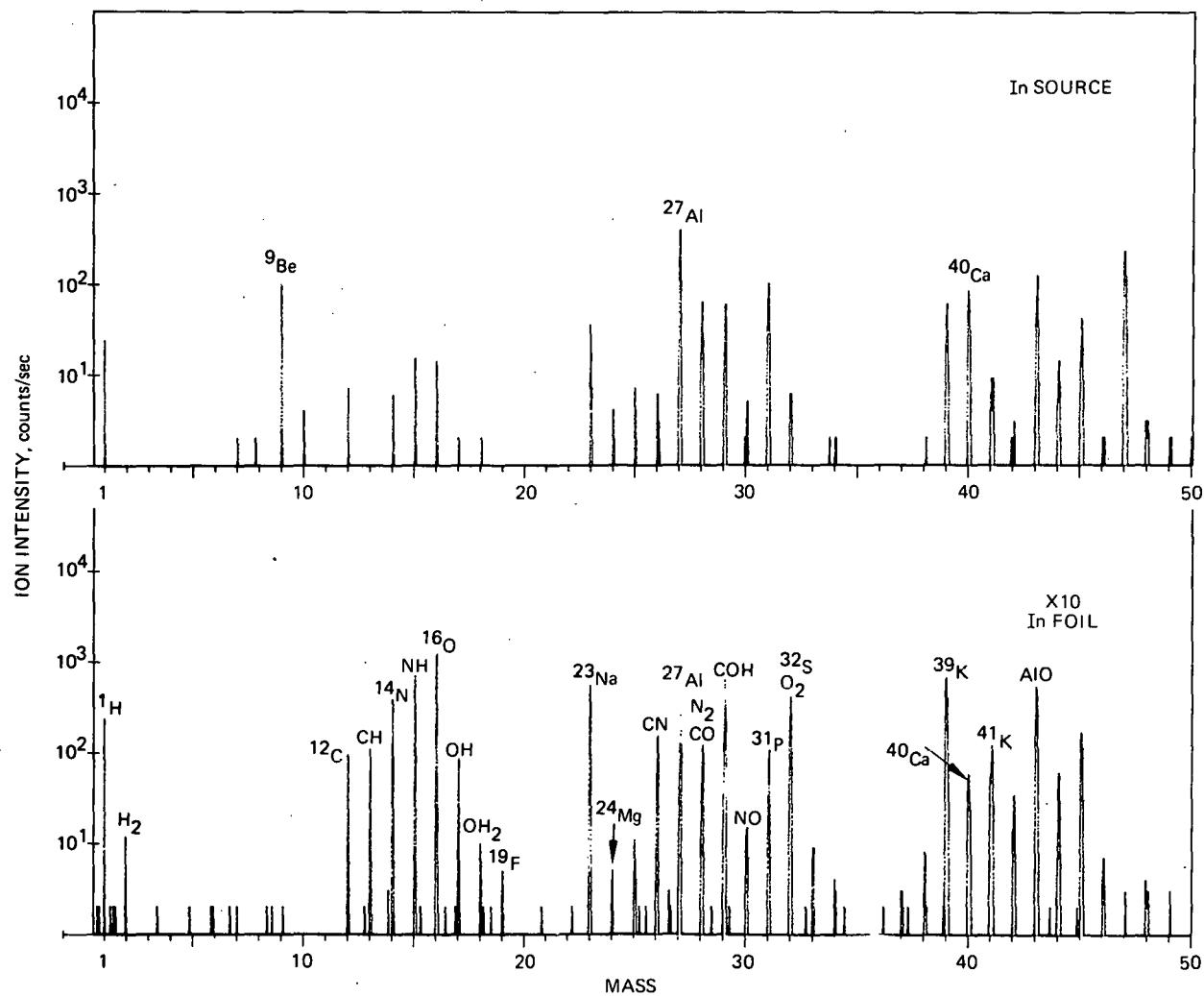


Figure 13(a). SIMS analysis of surface of In source and pure In foil for masses 1 through 50.

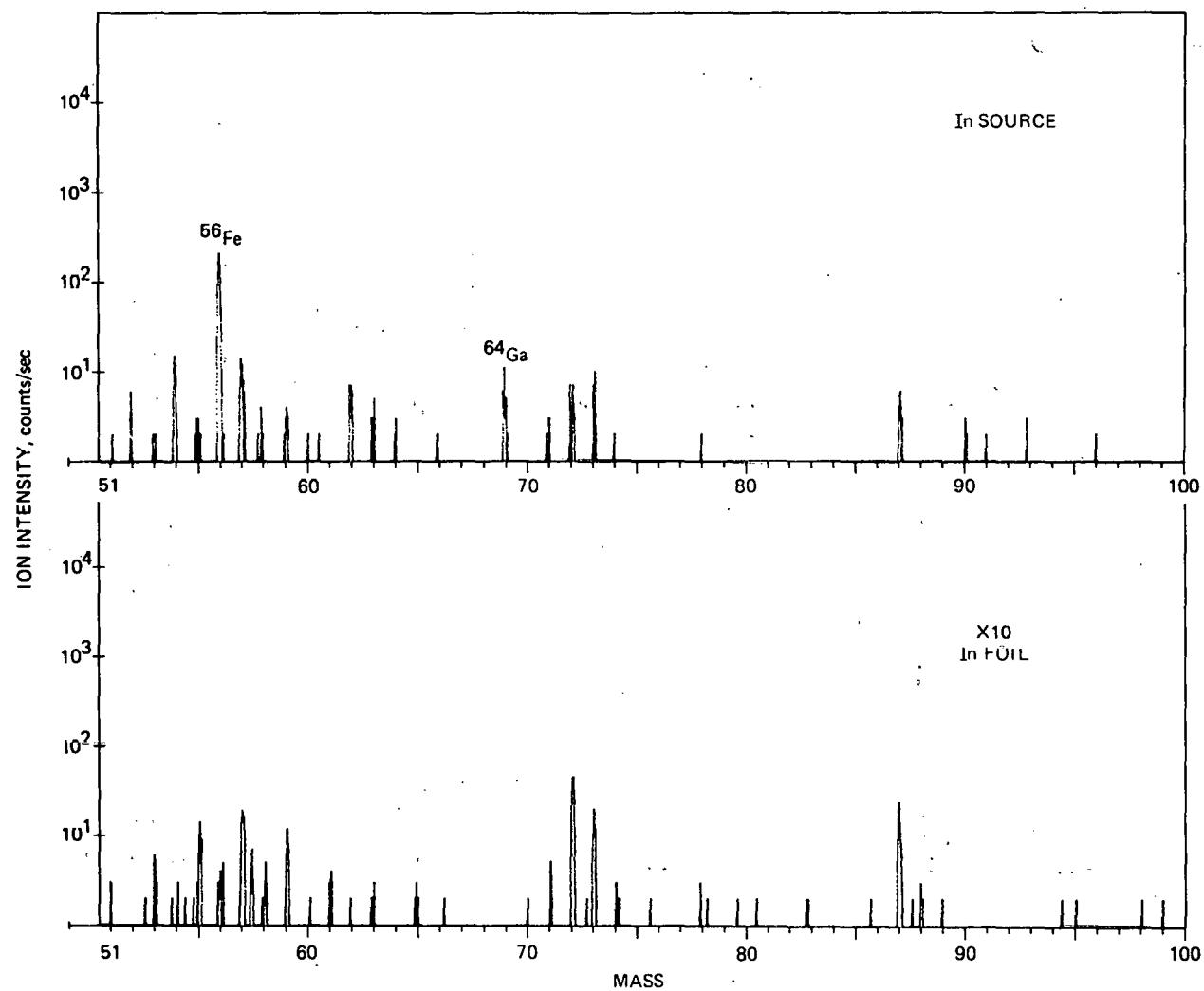


Figure 13(b). SIMS analysis of surface of In source and pure In foil for masses 51 through 100.

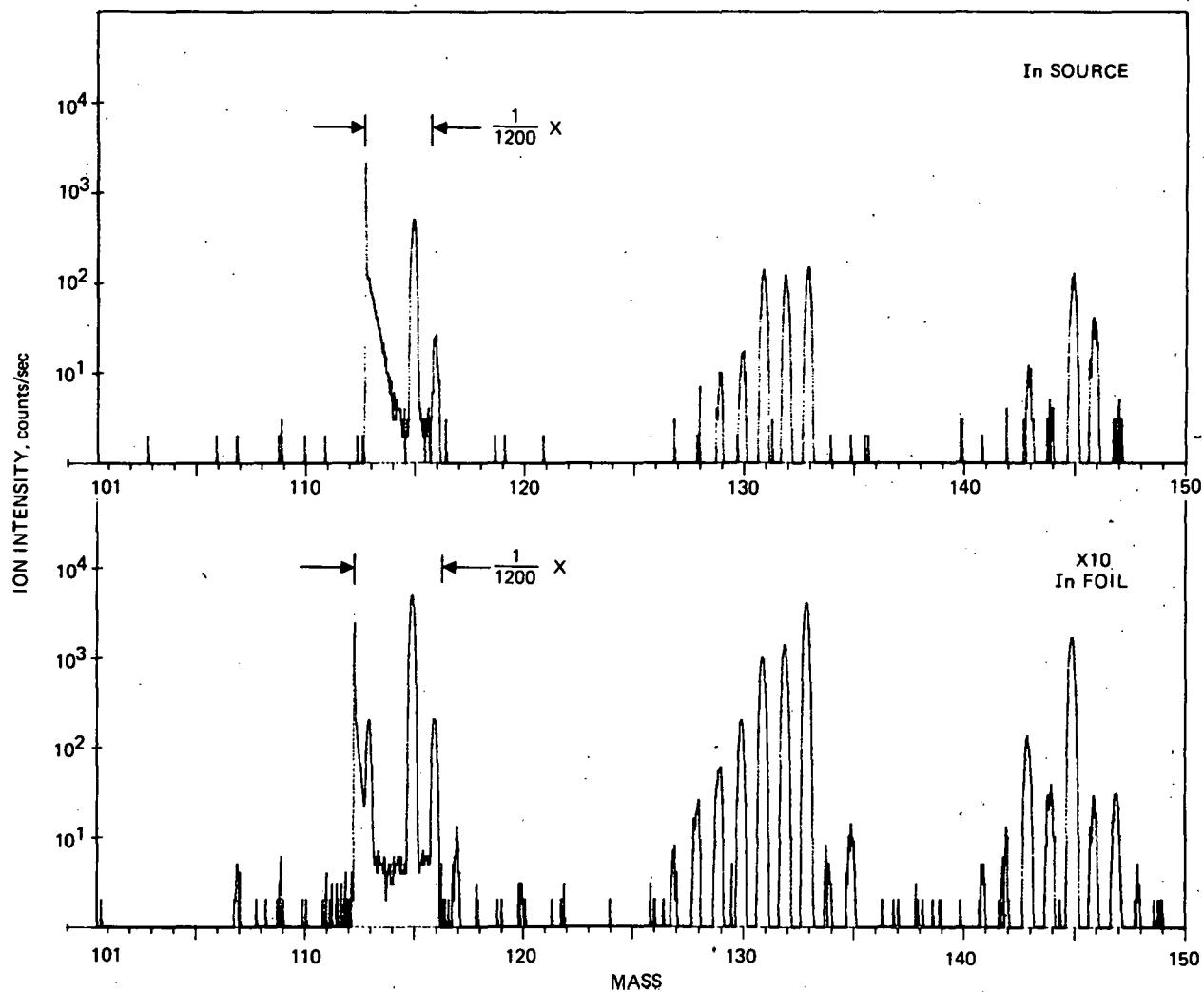


Figure 13(c). SIMS analysis of surface on In source and pure In foil for masses 101 through 150.

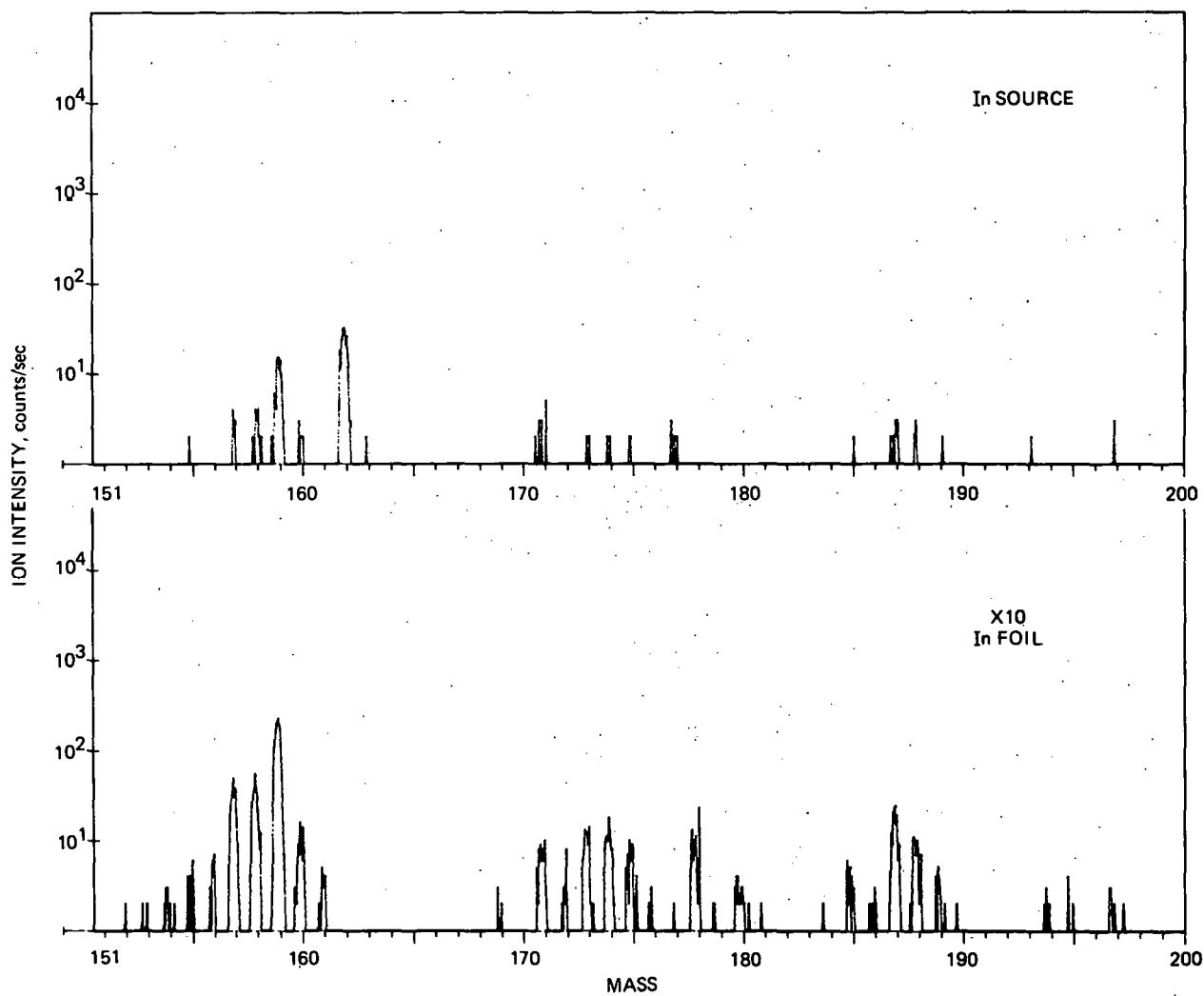


Figure 13(d). SIMS analysis of surface of In source and pure In foil for masses 151 through 200.

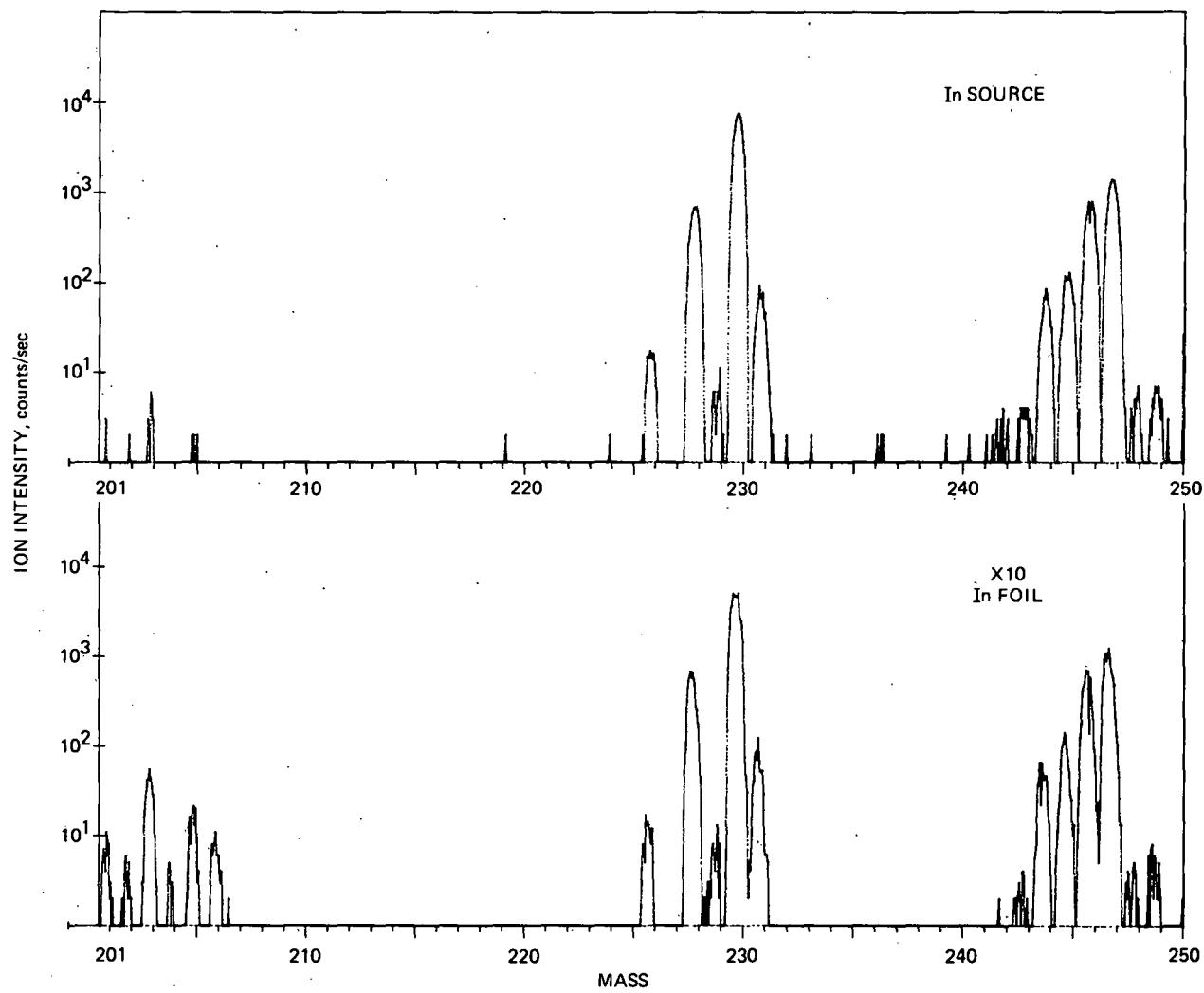


Figure 13(e). SIMS analysis of surface of In source and pure In foil for masses 201 through 250.

using an oxygen beam to excite secondary ions from an undoped In source. A mass spectrum (from masses 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 1,200 to be on the same scale as the remaining ions that 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 over the In foil are ^9Be , ^{27}Al , ^{56}Fe , and ^{69}Ga . A depth profile of these ions in the In source was then made (Figure 14). 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. We believe these impurity elements are in residual In in the PH_3 inlet line, which subsequently dopes the new source. Regardless, this level of Be does not change the films to p-type. InP prepared with this source was n-type.

Charles Evans & Associates have also done an Auger analysis at the surface of the InP source for P, C, and O. These elements were detected at the surface, and their concentrations fall below the level of sensitivity within a few hundred angstroms of the surface. Further studies are necessary to determine if repeated exposure of the source to air causes the oxidation.

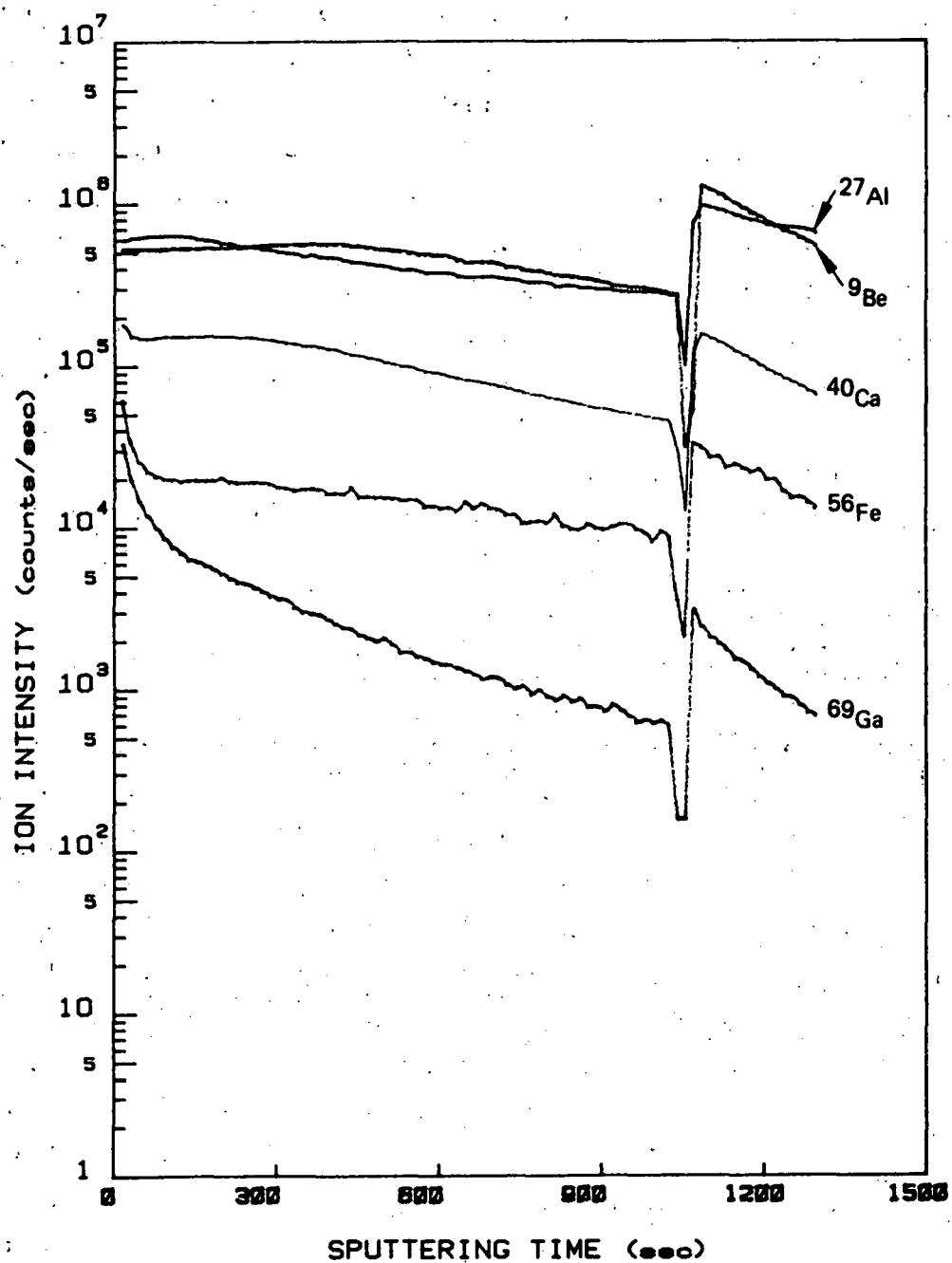


Figure 14. SIMS depth profile of ⁹Be, ²⁷Al, ⁴⁰Ca, ⁵⁶Fe, and ⁶⁹Ga in In source.

2. P-Type Films by 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, then inserted in the PH_3 inlet line just below the source, as shown in Figure 15. 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.

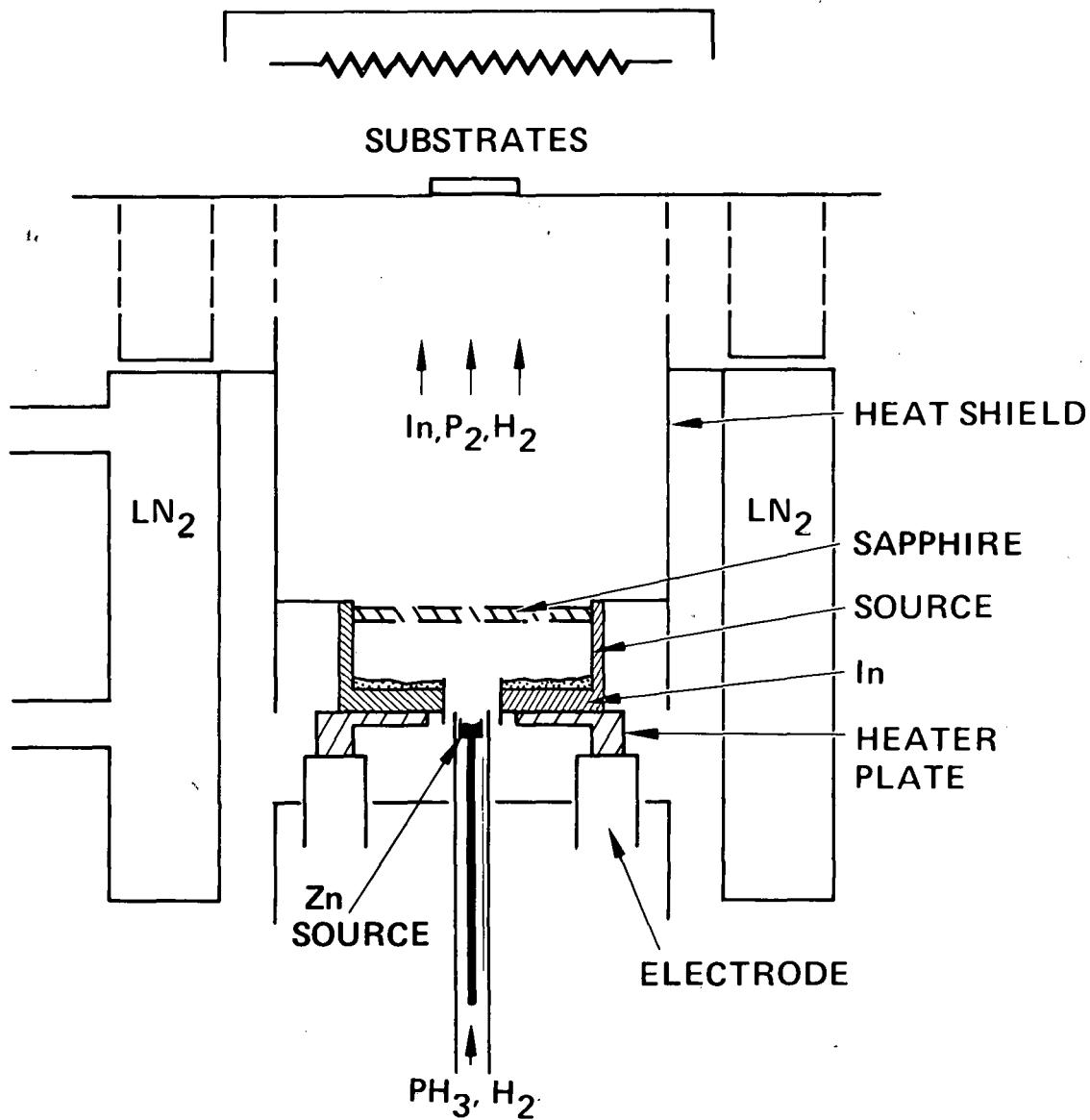


Figure 15. Zn-doping of InP prepared by PRD.

SECTION 4

ALTERNATIVE STRUCTURES

At a substrate temperature of 330°C , there are presently 10^{18} cm^{-3} n-type native defects present in our InP films. This background concentration is too high to permit good transport properties by overcompensation with p-type doping. At this substrate temperature the present morphology of the InP epitaxy is also inadequate. Figure 16 shows two InP/RXCdS structures, which, when considering the present material constraints, are possible for operation as efficient all-thin-film cells. In the first structure, a thin, $0.1 \mu\text{m}$ thick, n-type InP epitaxial film is deposited directly on the RXCdS substrate at 280°C or less. The purpose of this film is to provide a homojunction and act as a buffer layer to permit the subsequent epitaxial growth of p-type InP at a higher temperature. This approach eliminates the materials constraint of preparing an InP film on RXCdS, which must simultaneously contain large grains and be p type. To make this structure viable, it is necessary that $N_A + N_D$ be about 10^{17} cm^{-3} or less. Whether a $N_A + N_D$ of 10^{17} cm^{-3} or less can be achieved at about 300°C depends on the results of the studies in Section 3 which examine the effect of deviation from stoichiometry on the electrical properties.

The alternate approach in Figure 7 must be used if the background concentration of native defects cannot be reduced to 10^{17} cm^{-3} at 300°C or less where good epitaxy can be achieved. In this structure, an n^+ InP epitaxial layer is prepared at 280°C as in Figure 1. 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.

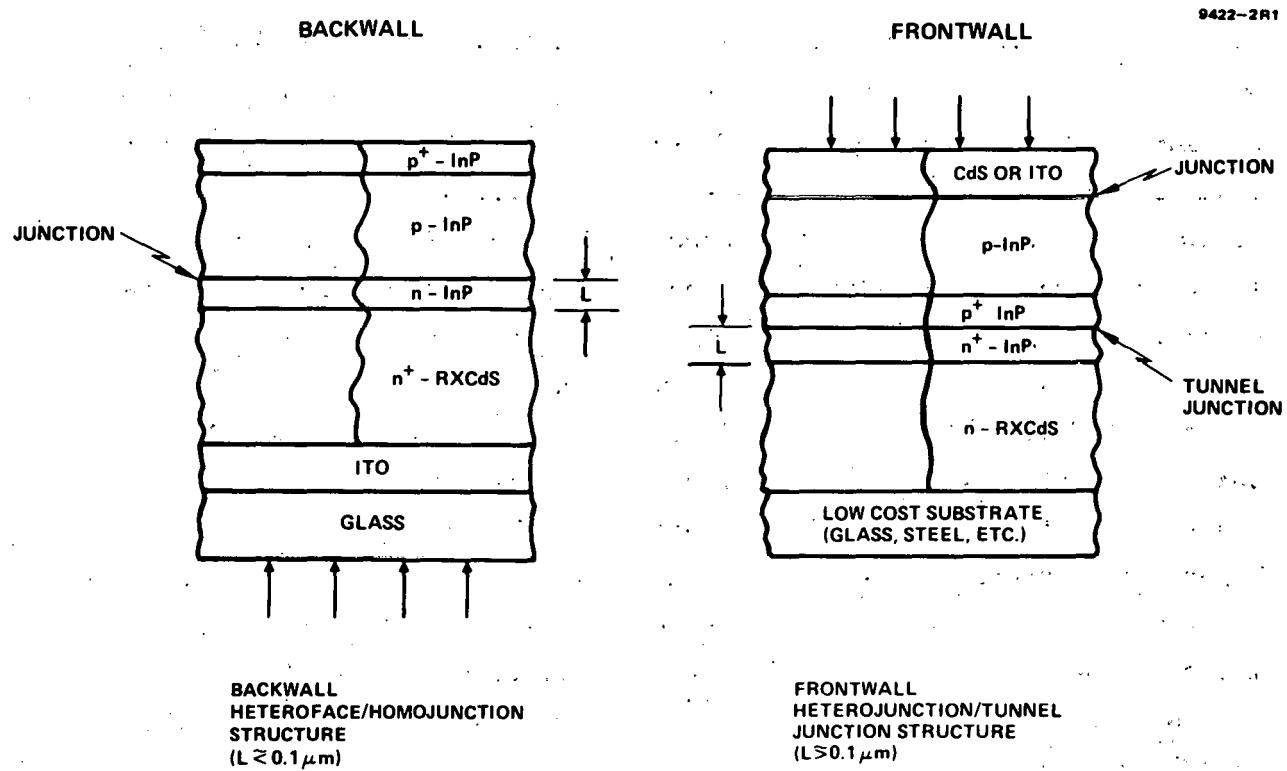


Figure 16. All-thin-film multilayer InP/CdS solar cells utilizing the backwall (left) and frontwall (right) structures.

SECTION 5

SUMMARY AND FUTURE WORK

In this period we grew InP on RXCdS at an intermediate substrate temperature of 330°C. The quality of the epitaxy was inadequate. Although SIMS showed the InP/CdS interdiffusion not to be serious, the SEM and x-ray Read pictures showed the InP grains to have both large and submicron dimensions. Extraneous nucleation of InP crystallites occur at this temperature. During the next period it will be necessary to vary the growth conditions, in particular, the RXCdS thermal etch procedure, and to vary the InP deviation from stoichiometry to increase the grain size.

Be-doped InP films were also grown on semi-insulating InP substrates at 330°C. However, consistent p-type doping was not achieved because of a high concentration 10^{18} cm^{-3} of n-type native defects. The concentration of native defects varies with the deviation from stoichiometry in GaAs grown by low-pressure techniques. Such a behavior is expected with InP. We began to vary $p_{\text{PH}_3}/F_{\text{In}}$ in our studies, and shall continue to do so in the next period to reduce the concentration of n-type native defects.

With continued use of the same Be/Al doped In source, the degree of p-type doping decreases. We believe this decrease is primarily a result of oxidation of the Be and Al at the surface of the In source, and consequently, a reduced flux of Be atoms. With SIMS analyses, we have confirmed the presence of Be in our InP films prepared from sources freshly charged with Be/Al alloys. We will extend these studies to films prepared with older sources. If the transient doping behavior with Be cannot be corrected, we will p-dope our film with Zn.

In the area of device fabrication, the first step will be to prepare a thin ($\approx 0.1 \mu\text{m}$) layer of epitaxial InP on RXCdS at about 280°C and evaluate that film. The second step will be to grow in succession, without breaking vacuum, the thin layer at 280°C and a 1- μm -thick p-type layer at a higher temperature ($\sim 350^\circ\text{C}$).

REFERENCES

1. N.G. Dhere and N.R. Parikh, J. Vac. Sci. Technology 17, 714(1980)
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, GaAs and Related Compounds 1978 Inst. Phys. Conf. Ser. 45 p.10.
5. Y. Seki, K. Tanno, K. Iida, and E. Ichiki, J. Electrochem, Soc. 122, 1108(1975).