

## PROGRESS IN $p^+n$ InP SOLAR CELLS FABRICATED BY THERMAL DIFFUSION

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### ABSTRACT

In this work we present the performance results of our most recently thermally diffused InP solar cells using the  $p^+n$  (Cd,S) structures. We have succeeded in fabricating cells with measured AMO, 25°C  $V_{oc}$  exceeding 880 mV (bare cells) which to the best of our knowledge is higher than previously reported  $V_{oc}$  values for any InP homojunction solar cells. The cells were fabricated by thinning the emitter, after Au-Zn front contacting, from its initial thickness of about 4.5  $\mu\text{m}$  to about 0.6  $\mu\text{m}$ . After thinning, the exposed surface of the emitter was passivated by a thin ( $\sim 50\text{\AA}$ ) P-rich oxide. Based on the measured EQY and  $J_{sc}$ - $V_{oc}$  characteristics of our experimental high  $V_{oc}$   $p^+n$  InP solar cells, we project that reducing the emitter thickness to 0.3  $\mu\text{m}$ , using an optimized AR coating, maintaining the surface hole concentration of  $3 \times 10^{18}\text{cm}^{-3}$ , reducing the grid shadowing from actual 10.55% to 6% and reducing the contact resistance will increase the actual measured 12.57% AMO 25°C efficiency to about 20.1%. By using our state-of-the-art  $p^+n$  structures which have a surface hole concentration of  $4 \times 10^{18}\text{cm}^{-3}$  and slightly improving the front surface passivation, we project an even higher practically achievable AMO, 25°C efficiency of 21.3%.

### INTRODUCTION

At the last SPRAT conference we predicted that for homojunction InP solar cells made by thermal diffusion the  $p^+n$  configuration has a higher efficiency than the  $n^+p$  configuration due especially to an increased  $V_{oc}$  (ref 1). The prediction was based on AMO, 25°C  $V_{oc}$  values of 860 mV we recorded for  $p^+n$  (Cd,S) InP solar cells as compared to experiment-based projected  $V_{oc}$  of only 840 mV for  $n^+p$  (S,Cd) InP solar cells. This value of  $V_{oc}$  for the  $n^+p$  (S,Cd) solar cells is in good agreement with previously predicted maximum  $V_{oc}$  values for thermally diffused  $n^+p$  (S,Zn) InP solar cells (ref 2).

Thermal diffusion is a desirable technique for homojunction InP solar cell fabrication because of its reduced complexity and a lower processing cost due to the possibility of large-scale batch processing of large-area devices. The drawback of this fabrication technique is that a large number of defects are present in the emitter layer after diffusion (ref 3), which makes the solar cell efficiency lower than that of solar cells fabricated by epitaxy, due especially to a lower open circuit voltage  $V_{oc}$ . In this paper we show how we have overcome this drawback and have achieved, to our knowledge, the highest  $V_{oc}$  for an InP homojunction solar cell.

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A significant improvement in the quality and radiation tolerance of InP structures fabricated by closed-ampoule thermal diffusion was obtained after optimizing the diffusion process using electrochemical (EC) techniques for step-by-step characterization of these structures during fabrication and after irradiation with high energy electrons and protons (ref 4). For our thermally diffused  $p^+n$  and  $n^+p$  InP structures, we found the ranking in decreasing order of projected maximum efficiency to be: 1)  $p^+n$  (Cd,S), 2)  $n^+p$  (S,Cd), 3)  $p^+n$  (Zn,S) and 4)  $n^+p$  (S,Zn). Based on experimental results we have projected a practically achievable AMO, 25°C efficiency of 21.3% for the  $p^+n$  (Cd,S) InP solar cell. A preliminary investigation of  $p^+n$  (Cd,S),  $n^+p$  (S,Cd) and  $p^+n$  (Zn,S) thermally diffused InP structures both prior to and after irradiation by high energy electrons and protons indicates that the same ranking holds for these three structures with respect to radiation tolerance as indicated above for maximum efficiency.

## EXPERIMENTAL

Cd and Zn diffusions into  $n$ -InP:S ( $N_D - N_A = 3.5 \times 10^{16} \text{cm}^{-3}$ ) were performed by a closed ampoule technique using high purity  $\text{Cd}_3\text{P}_3$  and  $\text{Zn}_3\text{P}_2$  (ref 5). Diffusion temperatures were from 500 to 550°C for Zn and from 560 to 660°C for Cd diffusion. The substrates were Czochralski LEC grown with an EPD of about  $5 \times 10^4 \text{cm}^{-2}$ . Diffusions were performed using a thin (40-50Å) phosphorus-rich chemical oxide diffusion cap layer (ref 1). Electrochemical techniques were used for step-by-step characterization of these diffused structures during fabrication and after irradiation with high energy protons (ref 3).

Small area (0.52  $\text{cm}^2$ )  $p^+n$  InP solar cells were fabricated on diffused structures with net surface acceptor concentration of  $3 \times 10^{18} \text{cm}^{-3}$ , diffused at 650°C. Au was used for the back contact and Au-Zn-Au (0.25  $\mu\text{m}$  thick) for the front contact. Since Au-Zn front contacts melt as far deep as over 3  $\mu\text{m}$  into the emitter during sintering at 430°C,  $p^+n$  structures with 4 to 5  $\mu\text{m}$  thick emitters were fabricated. Therefore, after front contact sintering, the emitters had to be thinned down over the uncontacted areas. Chemical thinning was employed using a new etchant which we call the "PNP" etchant (ref 6). No AR coating was used except for the thin (about 50Å) residual oxide which resulted from the thinning process. The front grid coverage was 10.55%. The 0.52  $\text{cm}^2$  total cell area was defined by mesa etching.

The solar cell performance parameters after thinning the emitter to different depths using this low etch rate PNP etchant were recorded at CSU using an ELH lamp after each thinning step. For selected cells, illuminated I-V measurements were done under AMO, 25°C conditions at NASA-LeRC. For these cells, dark I-V,  $I_{sc}$ - $V_{oc}$ , spectral response and temperature variation of performance parameters were also measured.

## RESULTS

At the last SPRAT conference we reported an AMO, 25°C,  $V_{oc}$  value of 860 mV for a  $p^+n$  (Cd,S) InP solar cell fabricated by closed ampoule thermal diffusion (ref 1). For an emitter thickness of about 0.25  $\mu\text{m}$  and using only a thin (~ 50Å thick) P-rich passivating layer as an AR coating, the  $J_{sc}$  value was 29.1  $\text{mA}/\text{cm}^2$ . From  $I_{sc}$ - $V_{oc}$  and spectral response measurements we calculated that by using an optimized ZnS/MgF<sub>2</sub> AR coating the expected  $V_{oc}$  and  $J_{sc}$  values for this cell would be 872 mV and 36.3  $\text{mA}/\text{cm}^2$ , which are higher than previously reported  $V_{oc}$  and  $J_{sc}$  values for  $p^+n$  InP structures fabricated by epitaxy (refs 7,8). However, a low FF of 52% was responsible for the low measured

AMO, 25°C efficiency of only 9.51%. The low FF was due both to a high contact resistance of our Au-Zn-Au front contacts and a large sheet resistance of about  $5 \times 10^3 \Omega\text{-cm}^2$  which resulted after thinning the emitter from an initial emitter thickness of about  $2 \mu\text{m}$  down to  $0.25 \mu\text{m}$ . The surface net acceptor concentration of these structures was  $1.5$  to  $2 \times 10^{18} \text{cm}^{-3}$ .

In order to reduce the series resistance  $R_s$  and therefore increase the FF we have concentrated our efforts on i) increasing the surface hole concentration, without altering the diffused structure quality and ii) find a good alternative for our Au-Zn-Au front contacts fabricated presently by E-beam evaporation such as to be able to deposit ohmic contacts on thin emitters without short-circuiting the junction.

A step-by-step electrochemical characterization of  $p^+n$  (Cd,S) structures as a function of processing parameters has enabled us to improve the fabrication process of diffused structures by reducing the structural and electrical-type defect density while increasing the surface net acceptor concentration (ref 4). As an example for structures with a net surface hole concentration of  $3 \times 10^{18} \text{cm}^{-3}$  (see Figure 1, curve A) we recorded EPDs as low as  $2 \times 10^2 \text{cm}^{-2}$ . The surface state density minima determined electrochemically after removing the front contamination layer ( $\sim 300 \text{\AA}$ ) from the surface of the lower surface concentration structure was below our measurable limit of  $10^{10} \text{eV}^{-1} \text{cm}^{-2}$ , while for the unoptimized higher surface concentration structure (curve B) was about  $2 \times 10^{10} \text{eV}^{-1} \text{cm}^{-2}$ .

Using these low defect density  $p^+n$  InP diffused structures with a net surface acceptor concentration of  $3 \times 10^{18} \text{cm}^{-3}$  (curve A, Figure 1) we have been able to fabricate cells with measured AMO, 25°C  $V_{oc}$  exceeding 880 mV (see Figure 2), which, to the best of our knowledge, is higher than previously reported  $V_{oc}$  values for any InP homojunction solar cell. The cells were fabricated by thinning the emitter from its initial thickness of about  $4.5 \mu\text{m}$  to about  $0.6 \mu\text{m}$  after Au-Zn front contacting. It was necessary to start with a thick emitter and to thin it down after sintering the front contacts because during sintering, the contact metallization penetrated about  $3 \mu\text{m}$  below the front surface. This has the drawback of reducing the surface hole concentration in the thinned emitter, thereby increasing the series resistance and lowering the fill factor. Figure 3 shows the external quantum efficiency (EQY) of this cell with a grid coverage of 10.55% and no AR coating. The low  $J_{sc}$  value of  $26.8 \text{ mA/cm}^2$  and the low EQY of this cell can be explained by the very large thickness of the emitter, a large grid coverage and the absence of an AR coating. The cell shows a surprisingly good blue response for an emitter as thick as  $0.62 \mu\text{m}$ , indicating a highly passivated surface with a very low recombination velocity. The cell had a high series resistance  $R_s$  of about  $3 \Omega\text{-cm}^2$  due to both high contact and sheet resistances, resulting in low fill factor (FF) of 73.1% and efficiency of 12.57%, respectively.

By further thinning the emitter, both  $V_{oc}$  and  $J_{sc}$  values increased, reaching a maximum of 884.6 mV and  $29.95 \text{ mA/cm}^2$  (bare cell) respectively, at an emitter thickness of  $0.3 \mu\text{m}$ . An increased  $R_s$  due to an increased emitter sheet resistivity produced a decrease in FF to 57.7% with a drop in efficiency to about 10.9%.

By using an optimized two layer AR coating, and reducing the grid shadowing to 6% the projected  $J_{sc}$  value for a  $0.3 \mu\text{m}$  thick emitter is about  $37.5 \text{ mA/cm}^2$ . From the  $I_{sc}$ - $V_{oc}$  characteristics (not shown) such an increase in  $J_{sc}$  will increase the  $V_{oc}$  by 10-11 mV, which means that the expected  $V_{oc}$  for these cells should be about 895 mV. Figure 4 shows the recorded temperature dependence of  $V_{oc}$  and efficiency for a  $p^+n$  InP cell after thinning the emitter to a thickness of about  $0.7 \mu\text{m}$ . An ELH lamp was used for illumination. The AMO  $V_{oc}$  and  $\eta$  values for this cell were 875.6 mV and 11.54%, respectively (bare surface). As far as we know, it is the first time a measured  $|\Delta V_{oc}/\Delta T|$  value below  $2 \text{ mV}/^\circ\text{C}$  is reported for an InP solar cell. This is not surprising since, as known, the theoretical value of  $|\Delta V_{oc}/\Delta T|$  decreases as the  $V_{oc}$  increases. Should it be possible to deposit ohmic front contacts on thin emitters (i.e. up to  $0.5 \mu\text{m}$  thick) without short-circuiting the junction, then the high surface hole concentration in the emitter would be preserved, and the projected FF of these cells should be about 82%

and the projected AMO, 25°C efficiency of 20.1%.

Our preliminary results using Au-Zn co-evaporation are very encouraging. After sintering at 350°C, for 1 minute 0.25 $\mu\text{m}$  thick Au-Zn contacts deposited by co-evaporation on a 0.6 $\mu\text{m}$  thick emitter with a net surface acceptor concentration of only  $1.5 \times 10^{18}\text{cm}^{-3}$ , gave an  $R_s$  value of about  $1.6\Omega\text{-cm}^2$  after thinning the emitter to 0.25 $\mu\text{m}$ . By comparison, using E-beam evaporated Au-Zn-Au of similar thickness, deposited on 3 $\mu\text{m}$  thick emitters with a similar surface concentration, after sintering for 2 minutes at 430°C and thinning the emitter to about 0.25 $\mu\text{m}$  gave an  $R_s$  value of  $10\Omega\text{-cm}^2$ , using the same photolithographically defined mask with a front contact coverage of 6.5%. The large increase is due especially to an increased sheet resistivity once the surface hole concentration drops below  $10^{18}\text{cm}^{-3}$ , which is what happens after thinning down thick emitters. The layered Au-Zn-Au contacts require thick emitters since the sintering temperature for forming ohmic contacts is about 430°C for 2 minutes and which causes after sintering the Au to penetrate the emitter at depths greater than 2 $\mu\text{m}$ .

If well controlled, we feel that co-evaporation, or better still, sputtering using premixed Au-Zn or Au-Cd targets, followed by a low temperature, short time sintering could be used for fabrication of good quality front ohmic contacts using thin emitters without short-circuiting the junction.

## DISCUSSION

Although not explicitly shown here, for our thermally diffused  $p^+n$  and  $n^+p$  InP structures, we found the ranking in decreasing order of projected maximum cell efficiency to be: (1)  $p^+n$  (Cd,S); (2)  $n^+p$  (S,Cd); (3)  $p^+n$  (S,Zn), and (4)  $n^+p$  (Zn,S). The performances of solar cells fabricated on these structures have shown that the same ranking holds. Except for the  $p^+n$  (Cd,S) cells the principal limiting factor for the other cell structures is  $V_{oc}$ . Experiment-based projected maximum achievable  $V_{oc}$  for our thermally diffused  $n^+p$  cells appears to be 840 mV, while for the  $p^+n$  (S,Zn) cell appears to be limited to about 860 mV. The large structural and electric-type defect density found in structures (2), (3) and (4) as compared to (1), namely, the  $p^+n$  (Cd,S) structure, explains their  $V_{oc}$  limitation. This possibly explains why although a relatively large experimental effort was made by NTT (Japan) to improve the  $V_{oc}$  and efficiency of diffused  $n^+p$  (S,Zn) cells the maximum reported AMO efficiency for these cells was of only 16.6% (ref 2) as compared to 19.1% reported for  $n^+p$  (Si,Zn) InP solar cells fabricated by MOCVD (ref 9).

As seen in Table 1, experiment-based (ref 10) projected maximum practically achievable efficiency for diffused  $n^+p$  (S,Cd) InP cells is of about 18.8%. A rather thick emitter of 0.08  $\mu\text{m}$  was considered in this case due to the fact that even at low diffusion temperatures (i.e., 600°C), a front phosphorus depleted dead layer is present at the surface. However, higher diffusion temperatures of 660 to 675°C are needed in order to increase the surface donor concentration. Owing to the graded nature of donor concentration profile, in this case, thinning the emitter below 800Å will decrease the surface concentration to below  $4 \times 10^{18}\text{cm}^{-3}$  which produces a decrease in  $V_{oc}$  and FF which upsets the  $J_{sc}$  increase.

The achievement of  $V_{oc}$  values for our diffused  $p^+n$  (Cd,S) bare cells, higher than those reported for epitaxially grown  $p^+n$  InP cells with optimized AR coating (refs 7,8) and even higher than that reported for all epitaxially grown  $n^+(\text{InGaAs})/n(\text{InP})/p(\text{InP})/p^+(\text{InP})$  solar cell of 876 mV which corresponds to the maximum reported AMO efficiency of 19.1% for an InP solar cell (ref 9), along with a high blue response, indicates that we have succeeded in overcoming the primary drawback of the thermal diffusion process, and we are able to obtain high quality reproducible  $p^+n$  diffused junctions with

very low bulk and surface defect densities in the emitter layer. As shown in the previous section, by reducing external losses, the projected AMO efficiency of cells fabricated on diffused  $p^+n$  (Cd,S) structures with a net surface concentration of  $3 \times 10^{18} \text{cm}^{-3}$  is 20.1%. As seen in Table 1, by using our state-of-the-art  $p^+n$  structures with a surface concentration of  $4 \times 10^{18} \text{cm}^{-3}$  (see Figure 1, curve B) we project the maximum achievable efficiency to be 21.3%. The relatively large increase in  $V_{\infty}$ , from our presently projected value of 895 mV to 910 mV, is based not only on a  $V_{\infty}$  increase with surface concentration but on our latest experimental data which show that further improvement in surface passivation is possible. Even higher  $V_{\infty}$  values, approaching 930 mV are possible by using better quality substrates (i.e. with EPD below  $10^4 \text{cm}^{-2}$ ), optimizing base doping, further optimizing the diffusion process and the quality of the passivating layer. Preliminary electrochemical investigation of our diffused  $p^+n$  (Cd,S),  $n^+p$  (S,Cd) and  $p^+n$  (Zn,S) InP structures prior to and after irradiating the structures by electrons and protons, included studies of carrier removal and structural and electrical-type defects introduced by irradiation, and appeared to indicate that the same ranking holds for these three structures with respect to radiation tolerance as indicated above for maximum efficiency. As an example, Figure 5 shows the variation in EC-V carrier concentration depth profiles as a result of irradiating  $p^+n$  (Cd,S) and  $p^+n$  (Zn,S) InP structures at a fluence of  $10^{13} \text{cm}^{-2}$  with 3 MeV protons. In this example, the  $p^+n$  (Zn,S) and  $p^+n$  (Cd,S) structures were diffused at 500 and 540°C and 560 and 650°C, respectively, using small amounts of source materials such that the surface dopant concentration was below the solubility limit of the diffusing species. This was done to decrease the density of diffusion-created defects such as surface and deep  $\text{Zn}_3\text{P}_2$  or  $\text{Cd}_3\text{P}_2$  precipitates and interstitial Zn or Cd. As seen, the carrier removal rates of  $p^+n$  (Cd,S) structures are significantly smaller than those of their  $p^+n$  (Zn,S) counterparts.

Since radiation resistance measurements are meaningful only when done on high efficiency solar cells, we have chosen to do them on our thermally diffused solar cells when we achieve BOL efficiencies of 18% or greater at 1 AMO, 25°C.

## CONCLUSIONS

By drastically reducing the defect densities of  $p^+n$  InP diffused structures we have succeeded in fabricating thermally diffused  $p^+n$  InP solar cells with measured AMO, 25°C  $V_{\infty}$  exceeding 880 mV (bare cells) which is higher than previously reported  $V_{\infty}$  values for any InP homojunction solar cells. Experiment-based projected maximum achievable AMO, 25°C efficiency of these cells is 21.3%.

For our thermally diffused structures the ranking in decreasing order of maximum efficiency is: 1)  $p^+n$  (Cd,S), 2)  $n^+p$  (S,Cd), 3)  $p^+n$  (Zn,S) and 4)  $n^+p$  (S,Zn). A preliminary investigation of  $p^+n$  (Cd,S),  $n^+p$  (S,Cd) and  $p^+n$  (Zn,S) InP structures both prior to and after irradiating by high energy electrons and protons indicates that the same ranking holds for these three structures with respect to radiation tolerance as indicated above for maximum efficiency. If this is correct, then  $p^+n$  (Cd,S) InP solar cells made by thermal diffusion can become very attractive for space applications due to a potential low cost, reduced complexity and adaptability to large scale batch processing.

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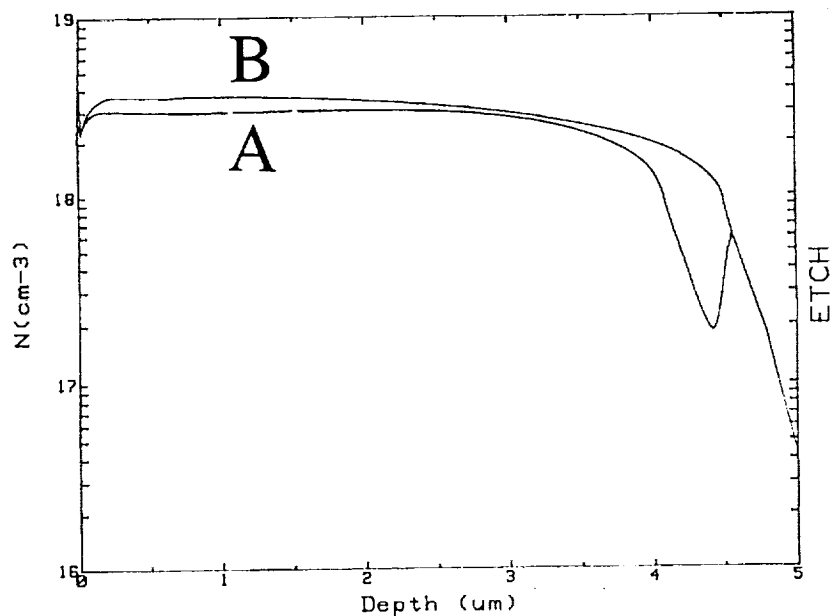


Figure 1. EC-V net acceptor concentration depth profiles of state-of-the-art thermally diffused  $p^+n(\text{Cd,S})$  InP structures. (A) Used for fabrication of cell in Fig.2; (B) High acceptor concentration structure to be used for our projected 21.3% efficiency cell (See Table 1).

Cell : 53  
 Date : 9 Oct 1992  
 Reference Cell : A-181  
 Area : .52 cm<sup>2</sup>  
 Temperature : 25°C  
 Air Mass Zero

I<sub>sc</sub> = 13.943 mA  
 V<sub>oc</sub> = 880.3 mV  
 I<sub>m</sub> = 12.78 mA  
 V<sub>m</sub> = 702.2 mV  
 P<sub>m</sub> = 8.975 mW  
 F.F. = 73.1  
 Eff. = 12.57 %

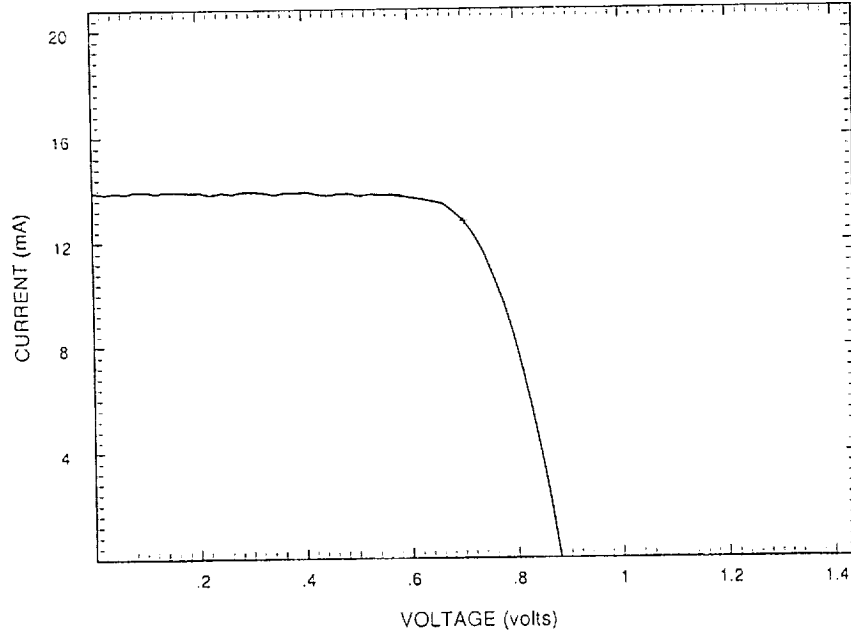


Figure 2. AM0, 25°C I-V characteristic of a p<sup>+</sup>n InP solar cell after thinning down the emitter from 4.5 μm to 0.62 μm. No AR coating; front contact coverage: 10.55%.

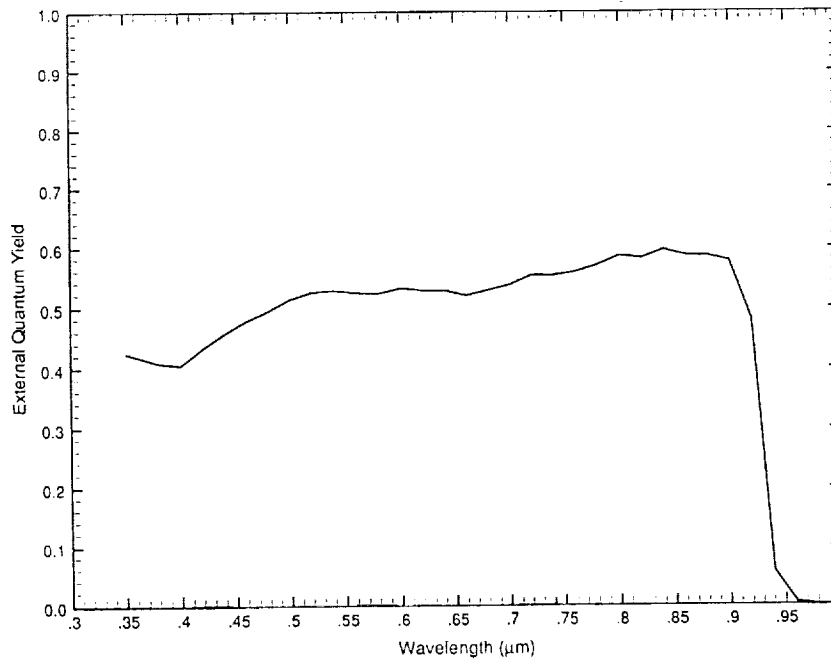


Figure 3. External Quantum Efficiency of cell in Fig. 2.

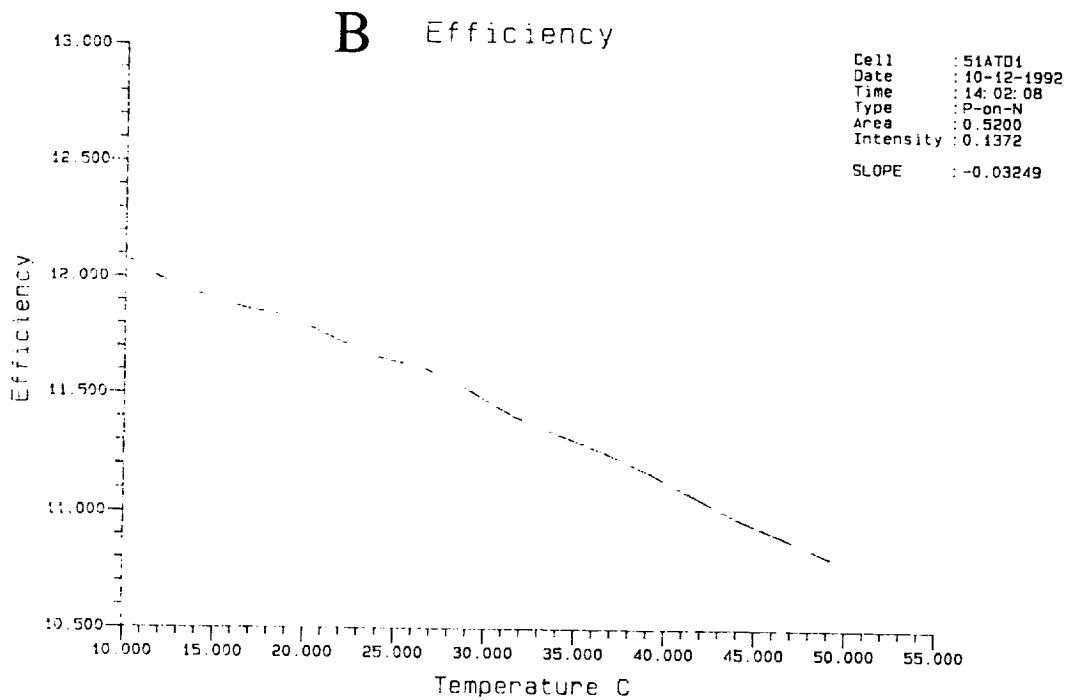
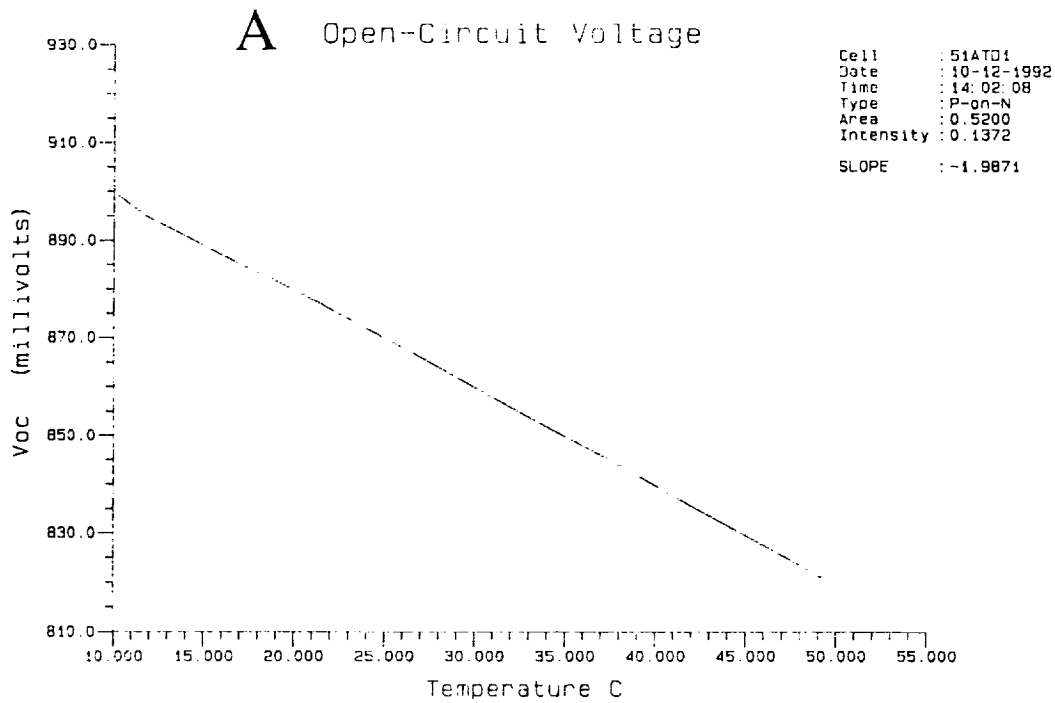


Figure 4. Temperature variation of  $V_{oc}$  (A) and efficiency (B) for a p<sup>+</sup>n (Cd,S) InP solar cell with no AR coating and emitter thickness of 0.7  $\mu\text{m}$ .



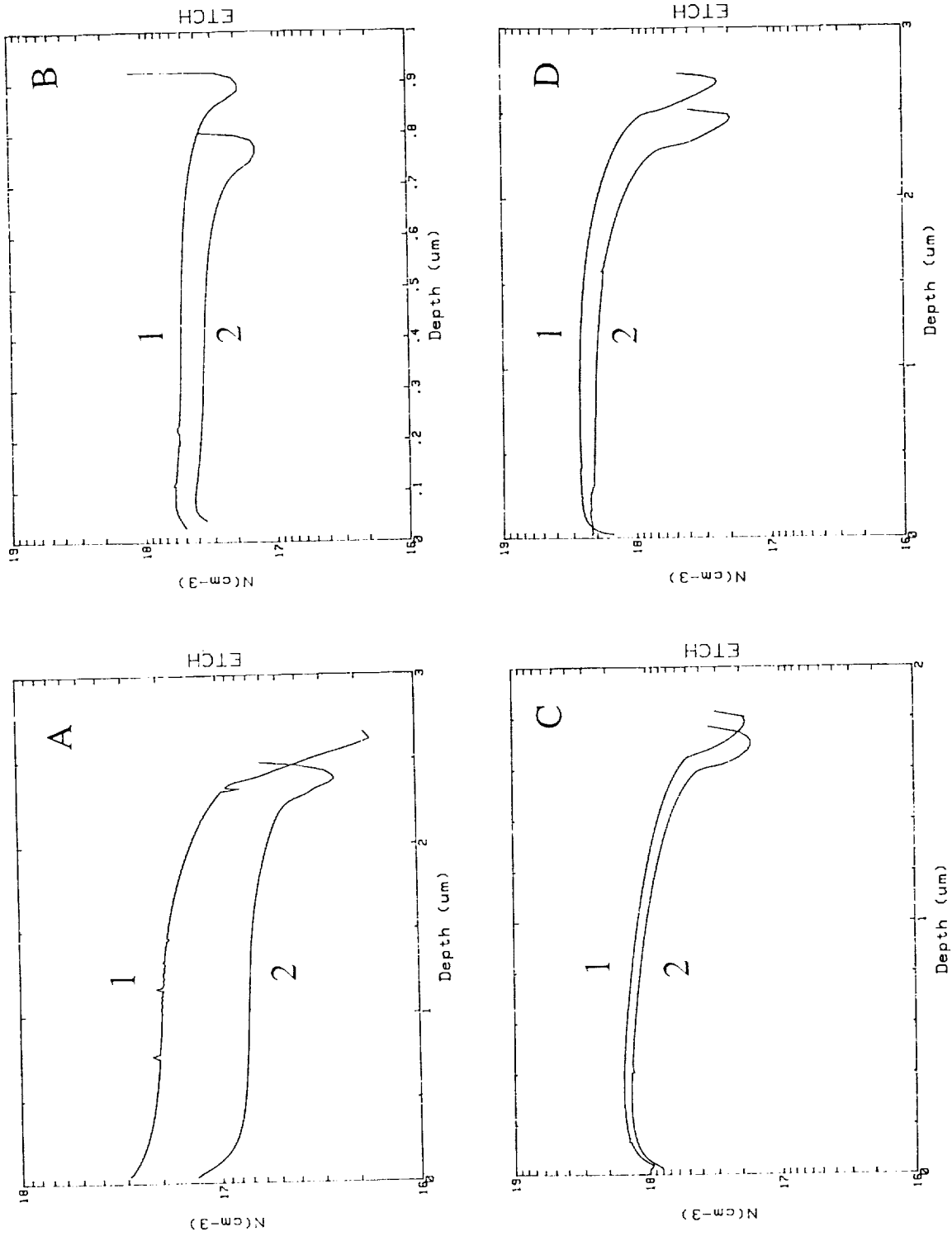


Figure 5. EC-V net acceptor carrier concentration prior to (curves 1) and after (curves 2) irradiating at a fluence of  $10^{13}/\text{cm}^2$  with 3MeV protons of InP(Zn,S) structures diffused at (A) 500°C and (B) at 540°C, and of InP(Cd,S) structures diffused at (C) 560°C and (D) at 650°C.

Table 1. Measured or Projected AMO, 25°C n/p and p/n InP Solar Cell Performances

Structure	Junction formation technique	Dopant	Approx Junction depth ( $\mu\text{m}$ )	$V_{oc}$ (mV)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	FF (%)	$\eta$ (%)	Ref.
$n^+(\text{InGaAs})/n(\text{InP})/p(\text{InP})/p^+(\text{InP})$	MOCVD	Si/Zn	0.025	876	36.34	82.4	19.1	[9]
$n^+p$	Closed Ampoule	S/Zn	0.2-0.3	828	33.7	81.6	16.6	[2]
$n^+p$	Closed Ampoule	S/Cd	0.15 0.08-0.1	806 840	30.5 36.5	80.1 84	14.35 <sup>(a)</sup> 18.8 <sup>(b)</sup>	[10]
$p^+i-n$	LPE	Mg/S	0.6	823.7	37.6 (active area)	75.4	17.2	[7]
$p^+(\text{InGaAs})/p^+(\text{InP})/n(\text{InP})/n^+(\text{InP})$	LPE MOCVD	Zn/S	0.7	866 864	29.25 32.84	81 76.7	15 15.9	[8]
$p^+n$	Closed Ampoule	Cd/S	0.25 0.62 0.3 0.25	860 880.3 895 910	29.1 26.8 37.5 38.2	52.2 73.1 82 84	9.52 12.57 <sup>(c)</sup> 20.1 <sup>(d)</sup> 21.3 <sup>(e)</sup>	[1] This work

(a) Measured on cells with unoptimized AR coating, and front contacts; (b) experimental-based projected maximum practically achievable performances; (c) Measured values on bare cell,  $R_s \sim 3\Omega \text{ cm}^2$ , front grid coverage: 10.55%; (d) Projected parameters of cell above by using an optimized AR coating, reducing the grid shadowing to 6% and reducing  $R_s$  to  $\sim 0.5\Omega \text{ cm}^2$ ; and (e) Maximum practically achievable projected parameters using our state-of-the-art diffused structures with a net surface acceptor concentration of  $4 \times 10^{18} \text{ cm}^{-3}$ .